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# Direct-Write of Sensor Devices by a Laser Forward Transfer Technique

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## ABSTRACT

The use of direct-write techniques in the design and manufacture of sensor devices provides a flexible approach for next generation commercial and defense sensor applications. Using a laser forward transfer technique, we have demonstrated the ability to rapidly prototype temperature, biological and chemical sensor devices. This process, known as matrix assisted pulsed laser evaporation direct-write or MAPLE DW is compatible with a broad class of materials ranging from metals and electronic ceramics to chemoselective polymers and biomaterials. Various types of miniature sensor designs have been fabricated incorporating different materials such as metals, polymers, biomaterials or composites as multilayers or discrete structures on a single substrate. The MAPLE DW process is computer controlled which allows the sensor design to be easily modified and adapted to any specific application. To illustrate the potential of this technique, a functional chemical sensor system is demonstrated by fabricating all the passive and sensor components by MAPLE DW on a polyimide substrate. Additional devices fabricated by MAPLE DW including biosensors and temperature sensors and their performance are shown to illustrate the breadth of MAPLE DW and how this technique may influence current and future sensor applications.

**Keywords:** MAPLE Direct-Write, Laser Transfer, Direct-Write of Sensor Materials, Temperature Sensors, Biological Sensors, Chemical Sensors, Chemiresistor.

## 1. INTRODUCTION

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 components. It also requires new strategies in order to eliminate the long lead times required for the fabrication of prototypes and evaluation of new materials and designs. In particular, for chemical and biological sensor development, the trend is toward the fabrication of micron scale devices and dense array platforms[1].

An individual chemical or biological sensor element consists of a transducer or substrate coated with one of a range of sorbent coating materials that collect the analyte of interest either in a reversible or irreversible binding process. Physicochemical changes in the sorbent coating, as a result of analyte binding events, are monitored and converted to electrical signals for display or recording. The range of sorbent materials covers a plethora of types and properties from simple polymers to higher-ordered biological structures. In order for these materials to perform as expected, their chemical and structural properties must remain uncompromised during the manufacture of the sensor[1]. In addition to the materials constraints, current commercial and military applications for chemical and biological sensors require systems to be portable (hand-held or smaller in size) so that analytical measurements can be made in the field. The above requirements have pushed traditional manufacturing techniques to their limits. Novel fabrication approaches for integrated micron sized sensor elements and systems are required.

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The use of direct-write techniques, that do not need photolithographic processing, provide a solution to the above constraints. 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 for modeling difficult circuits[2]. Examples of direct-write technologies for fabricating or modifying metallic interconnects and/or other electronic passive elements include ink jet printing[3], direct-write of ceramic slurries (Micropen©)[4], laser trimming[5] and laser chemical vapor deposition (LCVD)[6]. 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, multiple techniques are necessary to deposit and process the broad classes of materials employed in electronic and sensor applications.

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[7-10], phosphor materials[11], microbatteries[12,13] and even viable biomaterials[14,15]. In this paper, the use of the MAPLE DW technique for the fabrication of temperature, biological and chemical sensors is described. We compare the performance of chemiresistor gas sensors made by spray coating and by MAPLE DW. Finally, we demonstrate a complete chemical sensor system fabricated by MAPLE DW

## 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[6]. 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[14,15].

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 microns. 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 system.

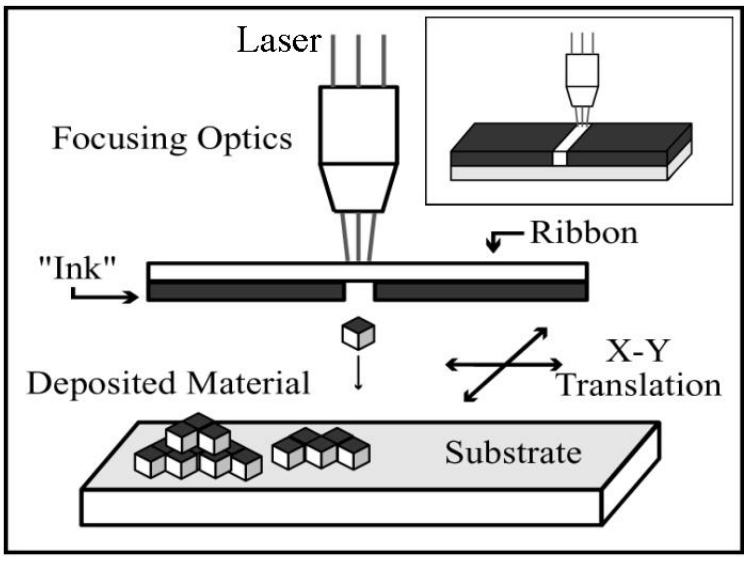


Figure 1. Schematic diagram illustrating the MAPLE DW process. Inset: the same setup can be used for micromachining with the ribbon removed.

## 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 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 15 μm thick. For the fabrication of the biosensor, a paste containing polyphenol oxidase, graphite and mineral oil was applied using the same wire-coater. In the case of the chemical sensors, the ribbons were prepared by spray coating a solution containing 0.1 gm of polyepichlorohydrin (PECH, average $M_W$ = 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, λ = 355 nm (Spectra Physics), was directed through a circular aperture and a 10x objective lens, resulting in a 85 μm 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 sensor fabrication and testing

Silver conductive lines were transferred by MAPLE DW onto polyimide substrates and used as temperature 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 °C on a hot plate to remove excess solvent and then cured at 280 °C in an oven for 10 min to decompose the organic silver precursors in order to form conductive patterns. These patterns in the form of serpentine lines were evaluated as temperature sensors by comparing their response to that 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 °C. The resistance of the serpentine was measured as a function of time using a computer controlled 34401A digital multimeter (Agilent).

### 3.3 Biosensor fabrication and testing

A 2 mm x 2 mm pad containing the biosensor mixture of polyphenol oxidase/mineral oil/graphite was deposited by MAPLE DW over Pt electrodes on a polyimide substrate. The resulting biosensor was immersed in a cathecol/water solution in order to measure the current generated across the Pt electrodes by the electrochemical reaction between the polyphenol oxidase and the cathecol. Details of the measurement are provided elsewhere[14]. Cyclic voltammetry measurements were performed using a PAR 263 potentiostat (EG&G) driven with M270 software.

### 3.4 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 exposing them to 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. The chemical integrity of the PECH polymer transfers was verified by FTIR using a Magna-IR 750 spectrophotometer (Nicolet). The spectra from 4 mm x 4 mm pads of pure PECH (no carbon) deposited by MAPLE DW onto NaCl discs was compared to that of a PECH films spray coated from a solution of PECH in chloroform.

## 4. RESULTS AND DISCUSSION

### 4.1 Temperature sensors

Physical sensors are essential for many aspects of manufacturing, medical and condition-based maintenance applications. These and other uses are pushing the development of physical sensors towards increased miniaturization and their integration within the physical structure of a part or component. However, most manufacturing processes are incapable of fabricating embedded sensors and instead the sensors are attached to the component being monitored. Due to the fragile nature of most sensor transducers, these tend to fail prematurely. Direct-write processes offer the ability to fabricate robust physical sensors embedded within the physical part in order to gather information regarding temperature, pressure, stress, torque, acceleration, wear, humidity, pH, etc. Such types of embedded physical sensors would find numerous uses for applications ranging from determining when a helicopter rotor shaft needs replacement to *in situ* monitoring with a surgical catheter.

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 100 ohms was made by MAPLE DW as shown in Figure 2(a). 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 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).

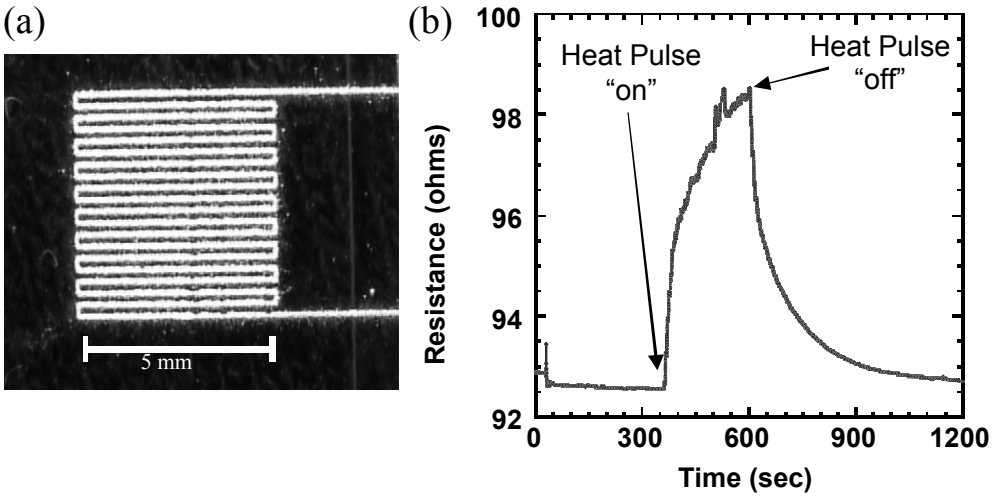


Figure 2. (a) Photograph of a temperature sensor made by MAPLE DW of a silver serpentine line on a polyimide substrate. (b) Response of this sensor to a heat pulse.

### 4.2 Dopamine biosensor

Wu et al.[14] demonstrated the fabrication of a simple amperometric biosensor for the detection of the neurotransmitter dopamine (a cathecol derivative) using MAPLE DW. The sensor operates due to the oxidation of dopamine to dopamine quinone in the presence of polyphenol oxidase. The reaction is electrochemically reversible in the presence of a suitable voltage across the electrodes, resulting in a current proportional to the dopamine concentration. The MAPLE DW transferred polyphenol oxidase/mineral oil/graphite pad is robust. The sensor does not show any signs of delamination or dissolution after several hours of operation immersed in an aqueous solution, indicative of good adhesion and inmobilization. Figure 3 shows a photograph of the biosensor element.

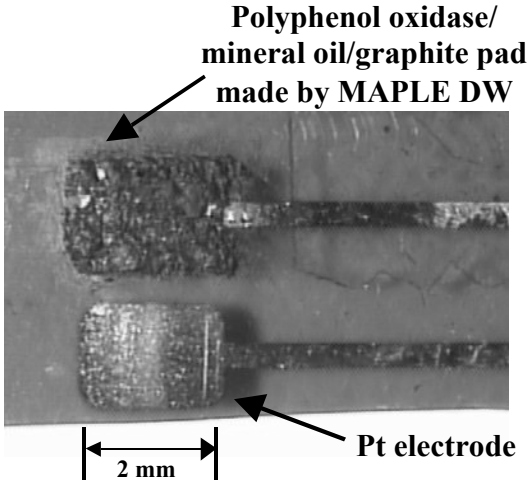


Figure 3. Amperometric biosensor made by MAPLE DW

**4.3 Chemiresistor gas sensors**

By using dispersions of conductive materials such as carbon and non-conductive chemoselective polymers, gas sensors based on conductimetric techniques[16,17] 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 schematically in Figure 4. 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.

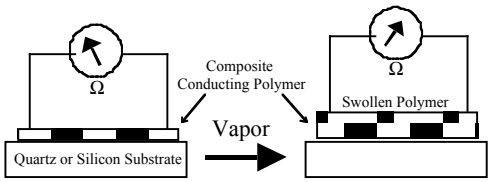


Figure 4. Schematic showing the basic operation of a chemiresistor gas sensor.

In order to determine if the chemical structure of the PECH polymer was affected by the MAPLE DW process, we compared the FTIR spectra of PECH films deposited by MAPLE DW and by spray coating onto NaCl substrates. The FTIR spectra of the spray coated PECH and MAPLE DW PECH are essentially identical with very similar stretching frequencies and absorbance ratios as shown in Figure 5.

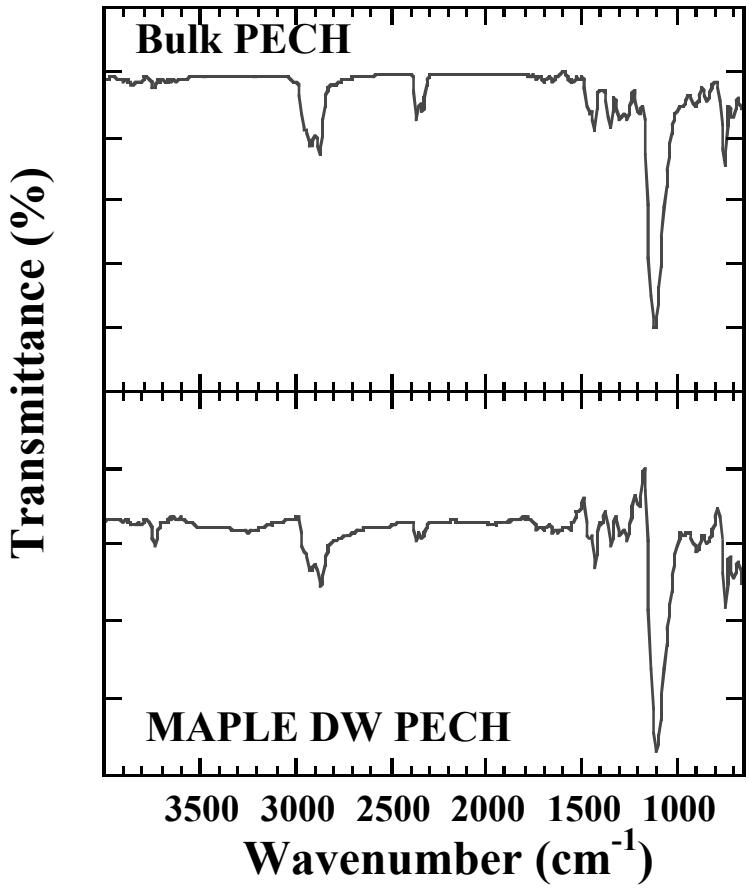


Figure 5. FTIR spectra from PECH films made by spray coating (bulk PECH) and by MAPLE DW on NaCl substrates.

Figure 6 shows a micrograph of a typical PECH/carbon chemoresistive pad fabricated by MAPLE DW across a set of silver interdigitated electrodes also made by MAPLE DW on a polyimide substrate. In order 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 anlytes. 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 chemoresisitors when exposed to various concentrations of toluene and DMMP vapors are shown in Figure 7.

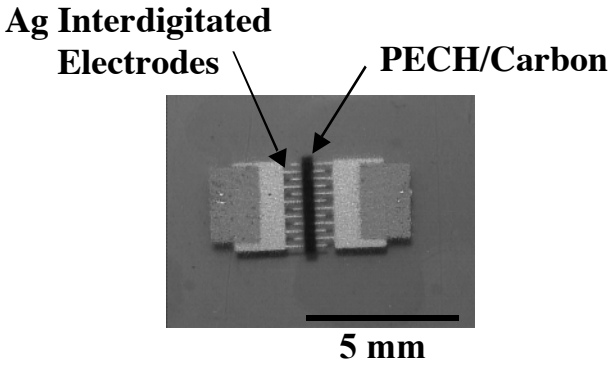


Figure 6. Optical micrograph of a chemiresistor gas sensor element made by MAPLE DW.

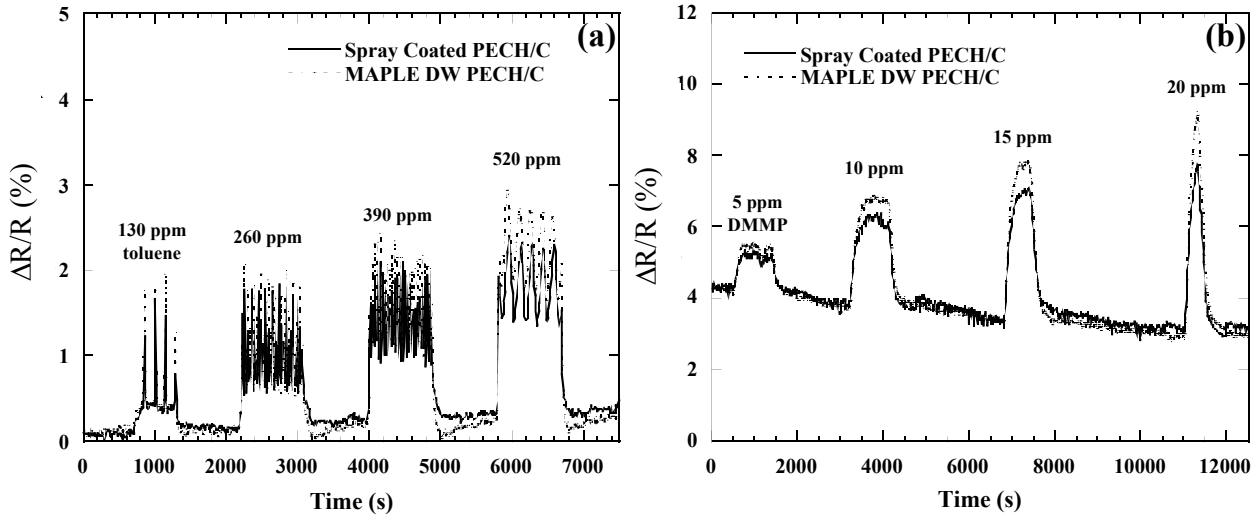


Figure 7. Response of a spray coated and a MAPLE DW PECH/carbon chemiresistor sensors to various concentrations of (a) toluene and (b) DMMP vapors. The spikes on the toluene response signals are due to the syringe pump system used to generate the calibrated vapor exposures.

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 8 which shows a photograph of a complete self contained chemical sensor system manufactured on a 5cm 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.

## 5. SUMMARY

MAPLE DW is an ideal process for the direct-write of sensors 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 numerous physical, chemical and biological sensor materials. MAPLE DW has been used for rapid prototyping of custom-engineered physical, biological and chemical sensors 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. Furthermore, in the case of chemiresistive gas chemical sensors, this work shows that the performance of the MAPLE DW sensor elements is comparable to that of similar sensors made by traditional manufacturing techniques.

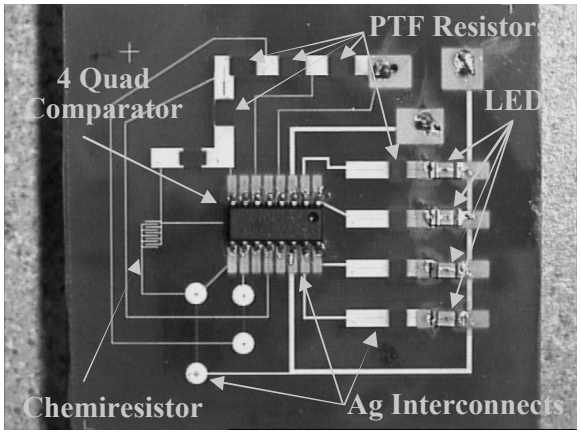


Figure 8. Photograph of a working chemiresistor sensor system made by MAPLE DW. The photograph shows all the elements of the sensor except for the batteries which are mounted on the back.

## 6. ACKNOWLEDGEMENTS

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## 7. REFERENCES

1. R.A. McGill, B. Ringeisen and P.K. Wu, "The Role of Direct Writing for Chemical and Biological Materials: Commercial and Military Applications", in *Direct-Write Technologies for Rapid Prototyping Applications*, edited by A. Piqué and D.B. Chrisey, p. 93, Academic, San Diego, 2001.
2. A. Piqué and D.B. Chrisey, editors, *Direct-Write Technologies for Rapid Prototyping Applications*, Academic, San Diego, 2001.
3. D.J. Hayes and D.B. Wallace, *SPIE Proceedings*, **2920**, 296, (1996).
4. 2. D. Dimos and P. Yang, *Proc. of 48th Electronic Components and Technology Conf.*, Seattle, Washington, p. 225 (IEEE, New York, 1998).
5. C.P. Christensen, M.T. Duignan and L.R. Rodriguez, *SPIE Proceedings*, **1835**, 128, (1993).
6. D.J. Ehrlich and J.Y. Tsao, editors. *Laser Microfabrication: Thin Film Processes and* Lithography, Academic, Boston, 1989.
7. A. Piqué, D.B. Chrisey, R.C.Y. Auyeung, S. Lakeou, R. Chung, R.A. McGill, P.K. Wu, M. Duignan, J. Fitz-Gerald, and H. D. Wu, *SPIE Proceedings*, **3618**, 330, (1999).
8. A. Piqué, D.B. Chrisey, R.C.Y. Auyeung, J. Fitz-Gerald, H.D. Wu, R.A. McGill, S. Lakeou, P.K. Wu, V. Nguyen and M. Duignan, *Appl. Phys. A*, **69**, S279 (1999).
9. D.B. Chrisey, A. Piqué, J.M. Fitz-Gerald, R.C.Y. Auyeung, R.A. McGill, H.D. Wu and M. Duignan, *Appl. Surf. Sci.*, **154**, 593 (2000).
10. A. Piqué, D.B. Chrisey, J.M. Fitz-Gerald, R.A. McGill, R.C.Y. Auyeung, H.D. Wu, S. Lakeou, V. Nguyen, R. Chung and M. Duignan, *J. Mater. Res*., **15**, 1872 (2000).

11. J.M. Fitz-Gerald, A. Piqué, D.B. Chrisey, P.D. Rack, M. Zeleznik, R.C.Y. Auyeung and S. Lakeou, *Appl. Phys. Lett.*, **76**, 1386 (2000).
12. K.E. Swider-Lyons, D.W. Weir, C.T. Love, R. Modi, T. Sutto, A. Piqué and D.B. Chrisey, *Power Sources for the Next Millenium*, edited by M. Jain, M.A. Ryan, S. Surampdi, R.A. Marsh and G. Nagrajan, Electrochem. Soc. Proc., **2000-22**, 272 (2000).
13. A. Piqué, K.E. Swider-Lyons, D.W. Weir, C.T. Love, R. Modi, *SPIE Proceedings*, **4274**, 317, (2001).
14. P.K. Wu, B. Ringeisen, J. Callahan, M. Brooks, D.M. Bubb, H.D. Wu, A. Piqué, B. Spargo, R. A. McGill and D.B. Chrisey, *Thin Solid Films*, **398-399**, 607 (2001).
15. B. Ringeisen, D.B. Chrisey, A. Piqué, H.D. Young, R. Modi, M. Bucaro, J. Jones-Meehan and B.J. Spargo, *Biomaterials*, **23**, 161 (2002).
16. J.W. Gardner, M. Craven, C. Dow, E.L. Hines, *Meas. Sci. Technol.*, **9**, 120 (1998).
17. J.V. Hatfield, P. Neaves, P.J. Hicks, K. Persaud, P. Travers, *Sens. Actuators B: Chem.*, **18**, 221 (1994).