Laser Direct-Write Techniques for Printing of Complex Materials

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Abstract

This article reviews recent developments in laser direct-write addition (LDW+) processes for printing complex materials. Various applications, ranging from small-scale energy storage and generation devices to tissue engineering, require the ability to deposit precise patterns of multicomponent and multiphase materials without degrading desirable properties such as porosity, homogeneity, or biological activity. Structurally complex inorganic materials for the successful fabrication of alkaline and lithium-based microbatteries, micro-ultracapacitors, and dye-sensitized micro solar cells are shown on various low-processing-temperature and flexible substrates using LDW+. In particular, the ability to deposit thick layers while maintaining pattern integrity allows devices produced in this manner to exhibit higher energy densities per unit area than can be achieved by traditional thin-film techniques. We then focus on more complex systems of living and biologically active materials. Patterns of biomaterials such as proteins, DNA, and even living cells can be printed using LDW+ with high spatial and volumetric resolution on the order of a picoliter or less, without compromising the viability of these delicate structures. These results provide for highly selective sensor arrays or cell seeding for tissue engineering. Finally, we review recent work on LDW+ of entire semiconductor circuits, showing the broad range of applications this technique enables.

Introduction

Laser forward-transfer techniques have become important direct-write alternatives to lithographic processes for generating high-resolution patterns. In these approaches, a pulsed laser is used to induce the transfer of material from a source film onto a substrate in close proximity to or in contact with the film. The source is typically a laser-transparent substrate that is coated with the material of interest, referred to in the literature as the target, donor, or ribbon. Laser pulses propagate through the transparent substrate and are absorbed by the film. Above an incident laser energy threshold, material is ejected from the source and propelled toward the acceptor, waiting, or receiving substrate. Translation of the source and receiving substrate, or scanning and modulating the laser beam, enables complex pattern formation in three dimensions with speed typically limited by the laser repetition rate. Commercially available, computer-controlled translation stages or galvanometric scanning mirrors enable rapid motion and high-resolution patterns from the individually written 3D volumetric pixels (voxels) that result from the laser forward-transfer process. Figure 1 shows a schematic illustrating the basic elements required for the laser forward-transfer apparatus. In contrast to many film deposition and patterning techniques, this approach does not necessarily require special vacuum or cleanroom equipment and can be performed under standard laboratory conditions.

One may consider these LDW+ techniques to be analogous to inkjet deposition of functional materials, without the constraints of a nozzle and with the added benefit of selectively using other laser processing techniques, such as laser direct-write modification (LDWM) and micromachining, or laser direct-write subtraction (LDW−), in the same tool. Also, in contrast to other LDW+ techniques, these approaches work on the principle of preserving the properties of the transferred materials rather than relying on a chemical reaction or other material modification to induce the deposition, as in laser chemical vapor deposition (see article in this issue by Stuke et al.). This added versatility in comparison with other printing methods enables LDW+ to manage the deposition and transfer of complex materials for which it is critical to maintain the delicate physical, biological, or chemical properties in the resulting patterns. Opportunities in fields ranging from metals deposition and power generation materials to biological and soft condensed matter abound. In this article, we will provide a brief overview of the use of LDW+ techniques for depositing complex material systems for applications in microelectronics, power generation, and biomaterials.

Laser-Induced Forward Transfer

The use of laser-induced forward transfer (LIFT) was first reported for the deposition of copper metal patterns inside a vacuum chamber.[1] Excimer laser pulses (λ=193 nm, 15 ns) were focused onto the back surface of a source substrate containing a thin copper film, producing a voxel of deposited material on the facing substrate. According to the proposed model for LIFT, the laser pulse heats the interface of the film at the source substrate, resulting in a melt front that propagates through the film until it reaches the free surface, at which time the material at the interface is superheated beyond its boiling point and the resulting vapor-induced pressure propels material forward toward the acceptor substrate[2] (see Figure 2a).

The LIFT technique is simple and can be used with a wide variety of solid film materials, mainly metals such as Cu and Ag,[3] Al,[4] W,[5,6] and Cr.[7] By accurately controlling the incident laser energy, submicron voxel features can be achieved.[8] Reports of LIFT for other materials such as Al_2O_3,[9] In_2O_3,[10] and even high-temperature superconductors[11] are worth mentioning, although the quality of the transferred ceramics is not as good as those deposited by traditional film growth techniques. The thickness of the transferred film on the acceptor substrate can be adjusted by repetitive transfers from the ribbon. In a similar way, multilayered structures can be deposited.

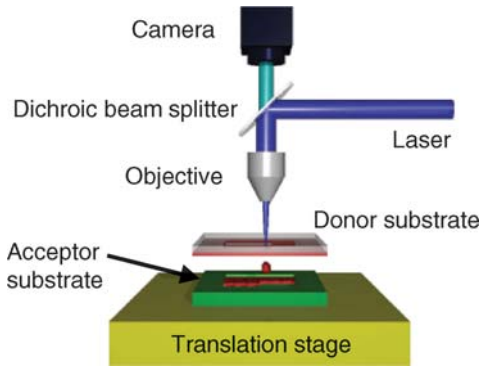

Figure 1. Schematic illustration of a laser direct-write addition (LDW+) forward-transfer apparatus. The laser is focused onto a layer of material mounted on the donor substrate. Ejected material is collected on the acceptor substrate, which can be manipulated by a translation stage. An imaging camera focuses through an objective to provide real-time monitoring of the process. Alternatively, the beam splitter can be replaced by a scanning galvanometer to translate the beam.

Traditional LIFT processing is sufficient in transferring simple materials that can be evaporated or melted, but for complex materials and instances where in order to preserve the properties of the material one needs to avoid such phase transformations, modifications to the process are necessary. Detrimental effects include oxidation or decomposition during transfer, formation of undesired phases upon recondensation of the transferred materials, or accumulation of high intrinsic stress of the rapidly quenched materials. Such problems are surmounted by the following three main variations of the original LIFT technique: (1) the use of a laser absorbing layer, or dynamic release layer; (2) the use of an absorbing matrix mixed with the starting material; and (3) the use of multicomponent, multiphase liquids or gel inks,

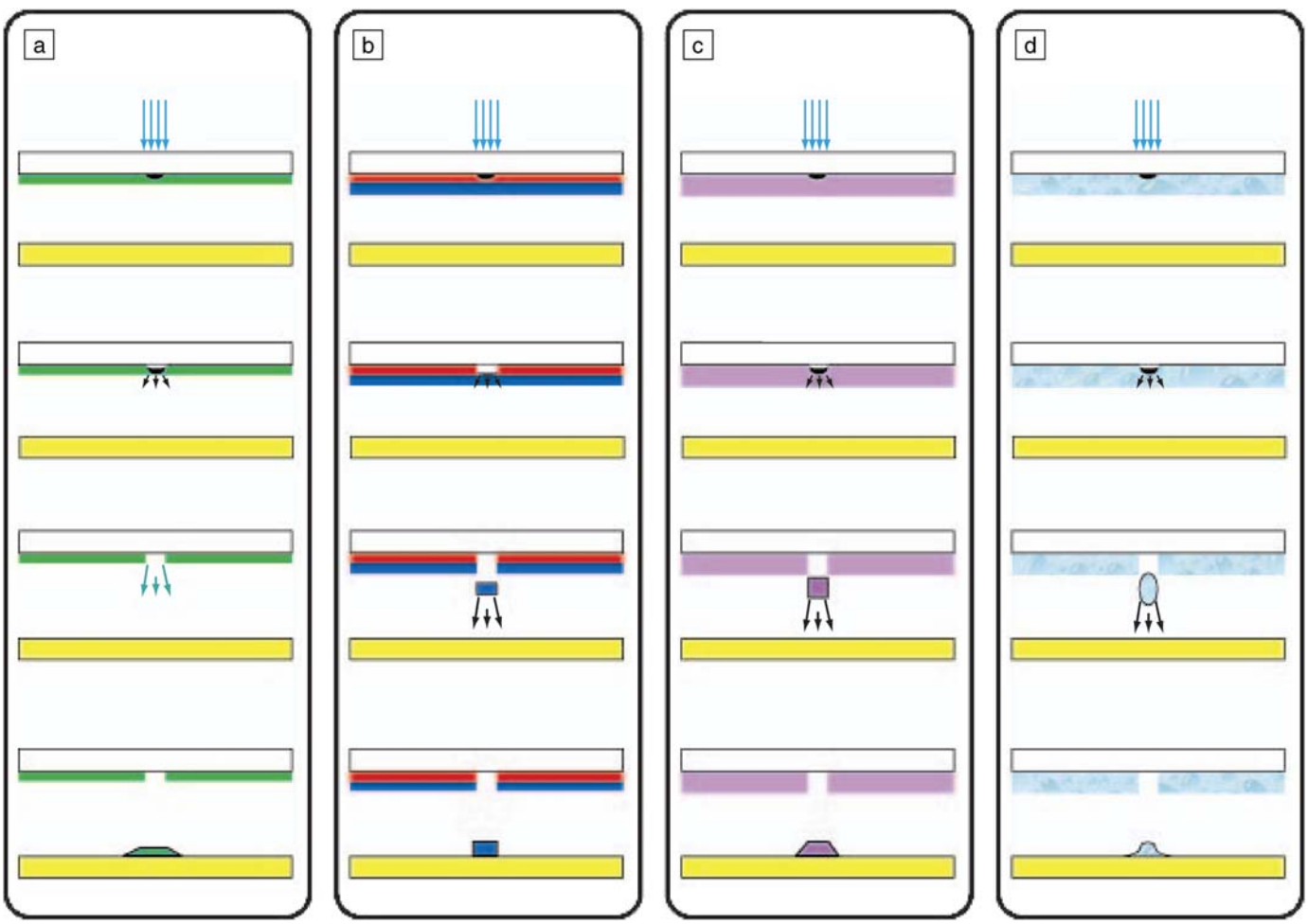

Figure 2. Schematic illustration of laser direct-write addition (LDW+) mechanisms. In all parts, the acceptor substrate is pictured in yellow. (a) Traditional laser-induced forward transfer (LIFT), in which the laser vaporizes the entire thin film in the region of laser focus. (b) LIFT with a dynamic release layer (DRL) (red) that is vaporized and propels the intact film (blue) forward. (c) Matrix-assisted pulsed laser evaporation direct-write (MAPLE-DW), in which the laser is absorbed by a sacrificial matrix (not shown) that must be removed after deposition. (d) LDW+ printing of rheological systems in which the laser is absorbed by a thin layer near the substrate and propels the remaining ink forward. The shape and nature of the deposited voxel can vary in the different methods.

generically referred to as rheological systems. These three general approaches are schematically represented in Figures 2b–2d. In reality, all three of these modifications represent an important difference from traditional LIFT technology, as functional materials are deposited without direct vaporization, which could affect their desirable physical, mechanical, or chemical properties upon condensation on the receiving substrate.

The work by Tolbert et al. using multilayered films demonstrates one of the first implementations of an absorbing layer in the LIFT process.[12] In this case, a thin layer, usually a metal, is deposited on the transparent support, followed by the material to be transferred. During LDW+, the laser pulse interacts with the absorbing layer, referred to as the dynamic release layer (DRL), causing it to vaporize in a similar manner as in LIFT (see Figure 2b). The confined vapor layer generates enough force to shear a block of material out of the second layer and toward the acceptor substrate. The advantage of this technique is that the transferred material has not evaporated or melted, and in general does not receive significant energy from the incident laser or experience a significant increase in temperature during transfer. Furthermore, materials with weak absorption of the laser radiation or materials that can be damaged by their interaction with the laser pulse can be accommodated by such an approach. The DRL, incident laser energy, and pulse shape can all be optimized so that the effects of the incident laser on the transferred materials are minimized.

Another variation of the LIFT process is to transfer various materials in powder form mixed with an organic or polymer binder. These mixtures or matrices are applied as a uniform coating on the transparent donor substrate (see Figure 2c). The properties of the matrix material are such that under laser irradiation, the binder absorbs the laser energy and is preferentially vaporized. This leaves the material of interest unharmed by the incident laser and allows for transfer to the receiving substrate. Subsequent processing such as LDWM or high-temperature oven annealing is required to remove any remaining binder that has not vaporized during transfer. Since this technique relies on a similar principle known as matrix-assisted pulsed laser evaporation (MAPLE), this technique has been called MAPLE-DW in the literature.[13,14] However, this term is sometimes used in the literature to loosely refer to LDW+ of any multicomponent system, regardless of the transfer mechanism.

One of the important advantages of MAPLE-DW over traditional LIFT is that thicker films can be deposited since the energy requirements to vaporize or shear the binder material are lower than those of a solid homogeneous film. Furthermore, the composite film is transferred in its solid phase, thus avoiding the melting and recondensation steps that take place in traditional LIFT. This modified LIFT approach has been used for the LDW+ of diamond nanopowders,[15] ferroelectric ($BaTiO_3$ and $SrTiO_3$) and ferrite ($Y_3Fe_5O_{12}$) micron-sized powders,[16] and carbon composite polymers for gas-sensing elements.[17]

A related approach is to move away from solid-phase binder materials toward multiphase and multicomponent liquid or gel systems. In these cases, the desired material is suspended or dissolved in a liquid to form an ink, which is then spread on the donor substrate (Figure 2d).[18,19] For metals and other common materials, screen-printing inks can be used. In this case, the laser interacts with all components in the source substrate, leading to vaporization of a portion of the ink, which then propels the remaining material toward the receiving substrate. Since only a small region of ink is required to absorb the laser energy, the transferred material remains unharmed by the incident laser. As with the previous approach, thick layers can be deposited and stacked. The higher volatility and relative ease in ejecting material from the ink mixture in comparison with various solid layers enables one to use small incident laser energies, which further protects the transferred materials from thermal damage. The fluid dynamics of the accelerating liquid results in flow during deposition that exhibits regimes of simple bubble expansion, complex explosive scattering, and even compact jetting behavior.[20] In addition, the use of inks enables the transferred materials to flow and coalesce, forming uniform and continuous coatings upon reaching the acceptor substrate. This eliminates one of the biggest drawbacks of traditional LIFT and other solid-phase transfer techniques in that interfaces between adjacent voxels can be minimized in order to create a more homogeneous transferred pattern. Furthermore, by allowing the deposited material to relax on the surface, conformal deposition on rough or curved surfaces or across steps of various heights is possible.[21,22] In moving to a wet or ink-based source, we will denote the method as LDW+ "printing" as a way to highlight the fundamental difference between this techniques and other LDW+ LIFT techniques.

LDW+ Printing of Complex Materials

An important feature of LDW+ printing is that the deposited materials typically exhibit porous structures with high surface areas. These properties can be beneficial for electrochemical applications where more complete contact between the electrodes and the electrolyte is desirable, therefore enabling better charge transfer and a more complete utilization of the electrode materials. Also, in some applications, the presence of an organic binder can actually benefit the properties of the transferred materials by making them more suitable for subsequent processing such as sintering. By combining features of the three techniques shown in Figures 2b–2d, such as using a DRL with a liquid solution or using a liquid-absorbing matrix, one can deposit new classes of materials such as living cells or biologically active materials. In contrast to most other liquid-based direct-write deposition techniques, the lack of a nozzle enables LDW+ printing to avoid many drying or clogging issues and accommodate highly acidic, caustic, or other chemically reactive materials, an important consideration for biological and electrochemical systems.

Given the diverse nature and large number of parameters affecting the LDW+ printing process, a simple model that fully describes the fundamental interactions between the laser and the transferred material is difficult to develop.[24] For instance, it is known that laser parameters such as fluence, pulse duration, pulse shape, and wavelength play an important role in the LDW+ printing process. Additionally, ink parameters such as the composition, thickness, viscosity, solids content, solids particle size, and where needed, DRL material and DRL thickness, greatly affect the ability to transfer a particular fluid and the resulting size and morphology of the transferred voxels. Parameters such as the distance between the donor and receiving substrates, substrate material, substrate temperature, and the surface chemistry and morphology of the substrate need to be considered as well. This wide parameter space for LDW+ printing leads to greater versatility in material choice than is available with other direct-write approaches. Furthermore, by optimizing laser and ink parameters, feature sizes on the order of 1–2 μm can be achieved.

LDW+ Printing of Energy Storage and Power Generating Systems

LDW+ printing has been used with great success in depositing materials for the fabrication of micropower sources, such

as ultracapacitors, batteries, and solar cells.[25–27] These electrochemical systems comprise three main internal components: a negative electrode or anode, a positive electrode or cathode, and an electrolyte/separator. Each of these components typically contains materials with a large degree of structural complexity, such as nanocomposites, solid-state polymers, liquids, or mesoporous mixtures of electrochemically active materials.[28] The fabrication of micropower sources represents the additional challenge of maintaining their electrochemical activity and structural integrity in a confined space while subject to the limitations, such as temperature and pressure, imposed by the microdevices, their substrates, and packaging.

One of the important attributes of LDW+ printing in the context of electrochemical systems is that it allows for the deposition of highly porous, multicomponent materials without modifying their properties. Figure 3 shows some examples in which the materials are single-component and porous, multicomponent with spherical inclusions, and multicomponent with plate-like structures. In all cases, the technique results in uniform transfer of the structurally complex materials with a porous structure that allows for good electrolyte penetration.

Another key advantage of LDW+ printing in constructing electrochemical cells is the flexibility in the design of operating geometries. The two main approaches include placing the anode and cathode adjacent to each other in the same plane (planar), or layering the anode and cathode on top of one another (stacked), with particular advantages and disadvantages to each of these designs. For instance, in the case of stacked geometries, one can obtain higher area densities and lower resistances, owing to the relatively thin separator layer, but this layer must be structurally stable enough to support the anode/cathode/current collectors. Furthermore, by combining LDW+ printing with LDW− to micromachine substrates, we can mitigate packaging difficulties by embedding the electrochemical components directly within a substrate, further reducing the packaged size of an entire microdevice while allowing their geometry to be adapted to fit virtually any form factor.[29]

Conceptually, the simplest system to construct in a direct-write manner is one in which the electrodes of the electrochemical cell are arranged adjacent to each other. For instance, an ultracapacitor or supercapacitor is a high-power-density component with a large specific capacitance whose voltage depends linearly on the stored charge, as in a standard capacitor. The chemistry of this system involves two identical electrodes composed of a hydrous metal oxide (hydrous ruthenium oxide) whose electrochemical performance is sensitive to the processing temperature.[30] Thus, we can use LDW+ printing to deposit a uniform layer of the hydrous ruthenium oxide powder mixed with the appropriate sulfuric acid electrolyte in order to reduce contamination.[23] LDWM and LDW− are used to temporarily dry the material and machine a small gap of approximately 10–20 μm in order to isolate two electrode pads, as shown in Figure 4a. The overall size and mass of these systems is small at <100 μg, while the power output is above 1 mW.[25] Such small-scale systems are ideal power delivery components for microdevice applications where size and weight are at a premium. For instance, remote sensors in security or defense applications and in civilian applications such as pollution monitoring or animal tracking are benefited by energy storage devices on this size scale.

In a similar fashion, planar alkaline microbatteries can be constructed.[31] In this case, shown in Figures 4b and 4c, the electrodes are composed of different materials such as Zn for the anode and Ag_2O as the cathode. The transfer process can use KOH electrolyte to form the inks and generate various planar geometries such as noncompact, interdigitated, or circular structures. LDW− is used to maintain electronic isolation and sharp interface structures. After fabrication, a droplet of KOH is added to the system to fully activate the cell. In this manner, 1.5 V batteries with an energy density of more than 0.6 mW h/cm^2 and specific energy of more than 160 mW h/g can be obtained.[32]

Although planar structures are relatively easy to construct, stacking the electrodes can provide a greater interface area for the battery structures and reduced contact resistance. One approach is to construct the electrodes on separate current collectors, using LDW+ printing, and manually assemble the layers.[33] However, by developing the appropriate inks and materials, one can use LDW+ to directly generate stacked structures that are rigid enough to support the upper layers without compromising the electrochemical performance. The use of a nanocomposite solid-polymer ionic liquid (nc-SPIL) enables such a construction approach, as this material has high ionic conductivity yet is chemically and structurally stable.[34] Figure 5 shows the basic geometry; we have used LDW+ to deposit sequential layers of cathode ($LiCoO_2$ or $LiMnO_4$), nc-SPIL, and anode (carbon) into a laser-micromachined pocket on a thin polyimide substrate for a Li-ion microbattery. This layered structure is significantly thicker (30–50 μm) than a typical thin-film microbattery structure (1–5 μm), yet thin enough to remain entirely embedded in the substrate. These

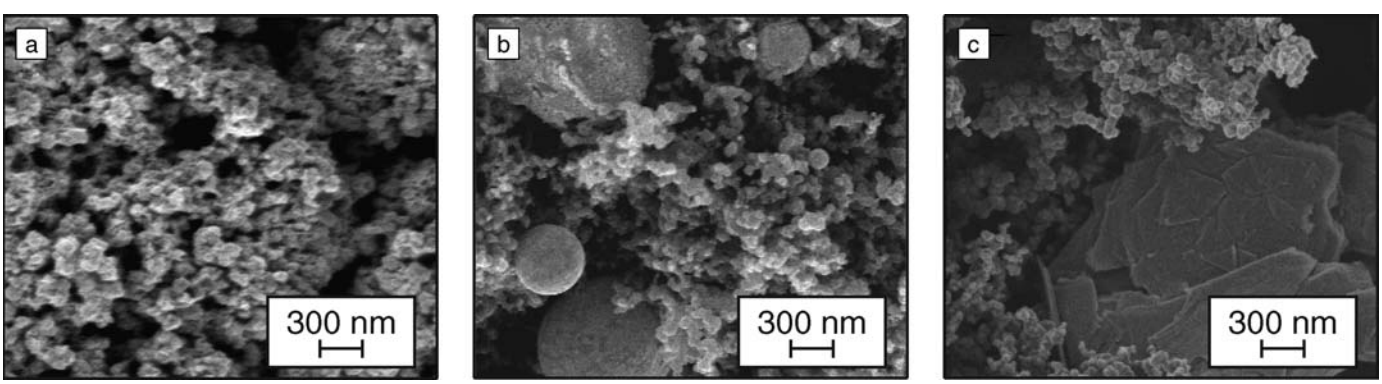

Figure 3. Scanning electron micrographs of LDW+ printing of electrochemical materials. (a) Single-component system of hydrous ruthenium oxide. (b) Mixed multicomponent system of silver oxide and carbon with spherical and rod-like particles. (c) Lithium cobalt oxide and carbon, a multicomponent system with flat, sheet-like particles of metal oxide.

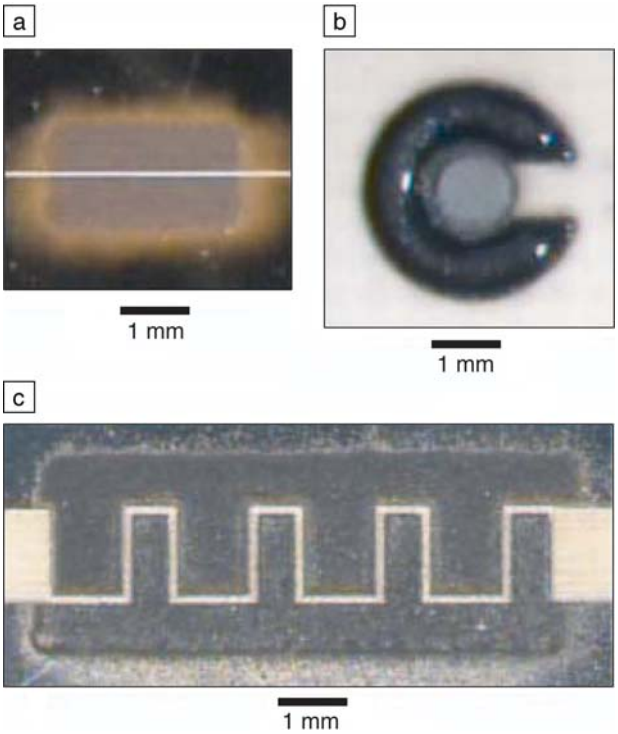

Figure 4. Examples of small-scale planar energy storage devices produced with laser direct-write. (a) Symmetric hydrous ruthenium oxide micro-ultracapacitor electrodes isolated with a 20-μm gap. (b) Circular alkaline microbattery. Central region is zinc; outer region is silver oxide. (c) Interdigitated alkaline microbattery with silver oxide top electrode and zinc bottom electrode. A combination of LDW+ and LDW− is used to create the patterns and maintain clean, sharp boundaries.

batteries are shown to be rechargeable for more than 100 cycles with an energy density of more than 1.3 mW h/cm^2.[35]

The final component in the development of a fully integrated micropower source is one with the ability to harvest energy from the environment to replenish the limited power supply of the microbatteries and ultracapacitors. Using the same combination of laser-based processes, we have begun to develop nanoparticle TiO_2-based solar cells.[27] LDWM allows local sintering of nanoparticles at low substrate temperatures to enable a large carrier lifetime without destroying the high-surface-area mesoporous structure. Photoelectrochemical cells showing greater than 4% conversion efficiencies, comparable to some organic photovoltaic materials but significantly less than the 20–30% efficiencies achievable by silicon-based photovoltaic materials, have been fabricated to date.

LDW+ Printing of Biomaterials

The ability to transfer or dispense microdroplets from a liquid suspension enables LDW+ printing to be an effective technique for patterning biological materials. Round-shaped and uniform micron-sized droplets of controlled diameters are obtained through the appropriate choice of both laser pulse energy and beam focusing conditions. Droplet volumes as low as 12 femtoliters have been achieved (Figure 6), providing a degree of spatial and volumetric resolution high enough to make LDW+ printing competitive for biomaterials against other direct-write techniques such as inkjet printing.[36] Furthermore, the fact that the amount of transferred material per laser pulse can be controlled through the characteristics of the laser beam (energy and spot dimensions) makes the use of nozzles unnecessary, thus avoiding potential clogging and contamination problems.

An important issue specific to LDW+ of biological solutions is their absorption properties with respect to the laser wavelength. Most biomaterials are dissolved in water-based solvents, making these solutions transparent to a wide range of common laser wavelengths, for instance, the second and third harmonics of a Nd:YAG laser, preventing laser transfer. For wavelengths that do absorb, one must be cautious not to denature the biomolecules due to thermal effects. Researchers have circumvented these difficulties by employing optical manipulation and laser-guided techniques to position cells,[37] or by using a biocompatible, sacrificial absorbing layer[12] deposited on the donor substrate, prior to source fabrication for LDW+ printing. Such techniques have a variety of names in the literature, such as biological laser printing (BioLP^{TM})[38] or absorbing-film-assisted LIFT (AFA-LIFT),[39] but in general, they work on the same LDW+ principle. More recent results have employed polymer-based absorbing layers that decompose upon laser irradiation, thereby preventing contamination of the transferred solution.[40]

The applicability of the laser-printing technique for biomaterials deposition is demonstrated through viability testing after transfer. Most tests rely on a fluorescence response of the biomaterial that will only be possible if the proper proteins and binding mechanisms are present. In the case of enzymes, catalysis of a reaction can be measured by staining for a particular chemical or other indicators. Laser printing of undamaged antibody anti-BSA (bovine serum albumin) on nitrocellulose has been demonstrated through fluorescence assays,[41] and immunostaining tests have demonstrated that biologically active 17 kDa antigens of *Treponema pallidum* can be successfully spotted onto nylon-coated slides through LDW+ printing.[42] Similar staining tests have revealed that this technique is adequate to deposit the enzyme alkaline phosphatase on nitrocellulose without altering its enzymatic properties.[43] Finally, the set of the most representative biomolecules is completed with DNA; fluorescence hybridization assays have revealed the correct deposition through the laser-printing of undamaged doublestranded DNA on poly-*L*-lysine–treated glass.[44]

More complex biomaterial systems such as living cells can be successfully transferred and patterned through LDW+ printing. The ability to print cells in an accurate and controlled manner has potential applications in such areas as tissue engineering, cell selection studies, and cell-based biosensors. It has been demonstrated that micron-sized patterns of bacteria[45] and several types of mammalian cells[40,46] can be deposited by means of laser printing. Figure 7 gives an example, showing an image of LDW+ printing of patterned *E. coli* bacteria that have been tagged with green fluorescent protein to indicate live cells after transfer.[47] In general, the viability of transferred cells has been tested

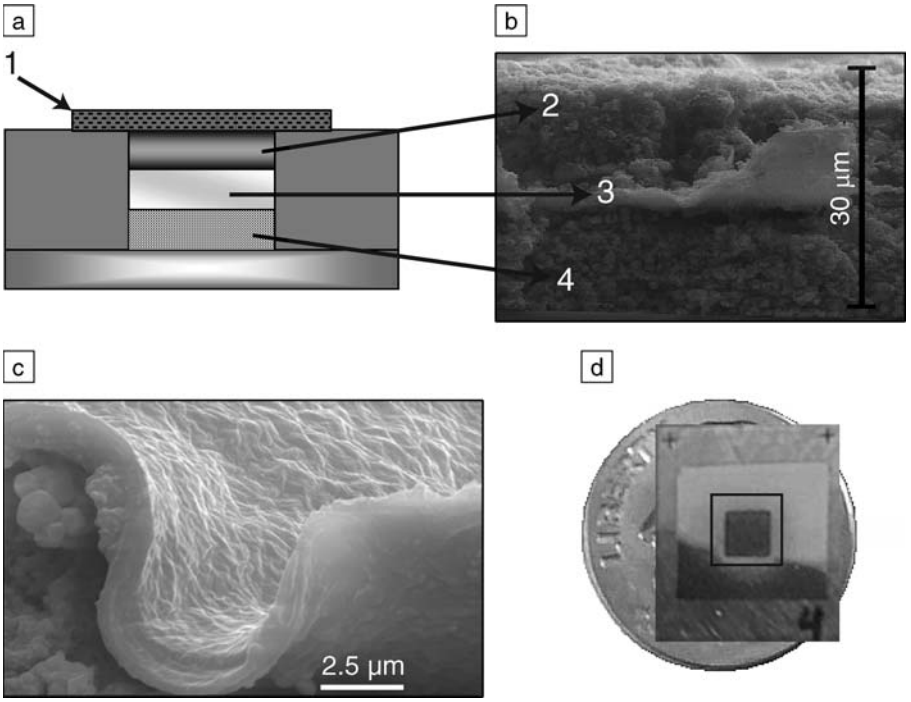

Figure 5. (a) Representative cross section and cutout schematic of an embedded lithium-ion microbattery fabricated by laser direct-write (LDW+) printing using a nanocomposite solid-polymer ionic liquid (nc-SPIL) electrolyte. (b) Scanning electron microscopy (SEM) cross section showing the layer structures. The numbers 1 through 4 correspond to the metal current collector, the carbon anode, the nc-SPIL electrolyte, and the lithium cobalt oxide, respectively. Layers 2, 3, and 4 are deposited sequentially by LDW+. (c) SEM images of the nc-SPIL separator with the cathode and anode removed, showing the structural integrity of the nc-SPIL after cleaving. (d) Actual LDW microbattery in a polyimide substrate shown against a U.S. dime for scale. The black square (3 mm × 3 mm) indicates the active battery portion of the system.

through diverse cell culture live/dead assays and immunocytochemical analyses, which have demonstrated that cells do not exhibit significant damage after the transfer process. One of the unique attributes of LDW+ printing for living cells is that the high degree of control, speed, accuracy, and spatial resolution enables controlled deposition of individual cells, a basic requirement in many pharmaceutical studies that cannot be achieved by traditional techniques.[46]

The ability to accurately place undamaged biomaterials onto solid substrates through LDW+ printing makes this technique an exciting tool for cutting-edge applications such as tissue engineering for wound repair and healing, manufacturing of miniaturized biosensors for parallel multianalyte detection *in vivo*, implantable drug delivery systems, and other applications where a controlled amount of solution and placement of cells with high resolution is required. For instance, the applicability of laser printing for biosensor preparation has been tested through the fabrication of a simple biosensor consisting of a DNA microarray capable of discriminating between two different DNA strands.[48] The microarray is prepared by depositing onto poly-*L*-lysine–treated glass droplets of three different solutions, two of them containing single DNA strands of a different human gene each and the other containing the control solvent (Figure 8a). Fluorescence analyses after hybridization with the complementary base sequences, each tagged with a different fluorochrome, reveals that the microarray is fully functional and selective in biomolecule detection (Figure 8b).[49]

Laser Transfer and Embedding of Electronic Components and Devices

In the same manner that LDW+ printing can transfer the complete biological system of a living cell, a similar process can be used to deposit complete electronic systems. The use of LIFT processes for the transfer and placement of prefabricated parts of components onto a receiving substrate was first reported by Holmes et al.[50] In their work, the authors describe the laser-driven release of Si-based microstructures from a UV-transparent substrate with an intermediate polymer sacrificial layer. Upon irradiation with an excimer laser pulse, a thin fraction of the sacrificial layer is vaporized, releasing the microstructure. This technique was later used to demonstrate laser-assisted assembly of microelectromechanical devices from parts fabricated on separate substrates.[51] These initial results confirm LDW as an alternative to conventional "pick-and-place" approaches for the placement of electronic components such as passives and semiconductor bare dies. The basic concept is similar to the DRL used in the transfer of biomaterials. By applying a sacrificial layer, such as the polymer layer used by Holmes, to attach the individual components to a UV-transparent support, the laser pulse ablates the sacrificial layer, generating gases that release and propel the component toward a receiving substrate placed in close proximity. This laser device transfer is a contactless process and thus allows the transfer of very small and very thin components that could easily be damaged by "pick-and-place" tools.

In applying this technique to more complex semiconductor systems, we have recently demonstrated that it is possible to transfer complete bare die circuits with the active surfaces facing up.[52] This added benefit of LDW enables other LDW+ processes to make contact with the device. The challenge, however, is to illuminate the active region of the die with the transfer laser pulse without damaging it. We have recently demonstrated this capability with the laser forward transfer of individual InGaN LED bare dies (250 μm × 350 μm) using a series of low-fluence UV laser pulses (~150 mJ/cm^2). Once laser-transferred, the LEDs are electrically tested and their operation verified.

We have also demonstrated the use of LDW techniques for the fabrication of embedded electronic circuits.[53,54] In this work, a simple blinker circuit comprising six passive surface-mount devices (4 resistors and 2 capacitors), two LEDs, and one unpackaged integrated circuit (LM555 chipset in bare die form) is embedded in a thermoplastic polyetherimide substrate using LDW. LDW− micromachining is used to generate pockets in the substrate in which each component is buried. Once in place, the components are encapsulated under a layer of polyimide. The interconnects required by the circuit are made by laser-micromachining vias in the protective layer to expose the contact pads on each device, through which LDW+ printing

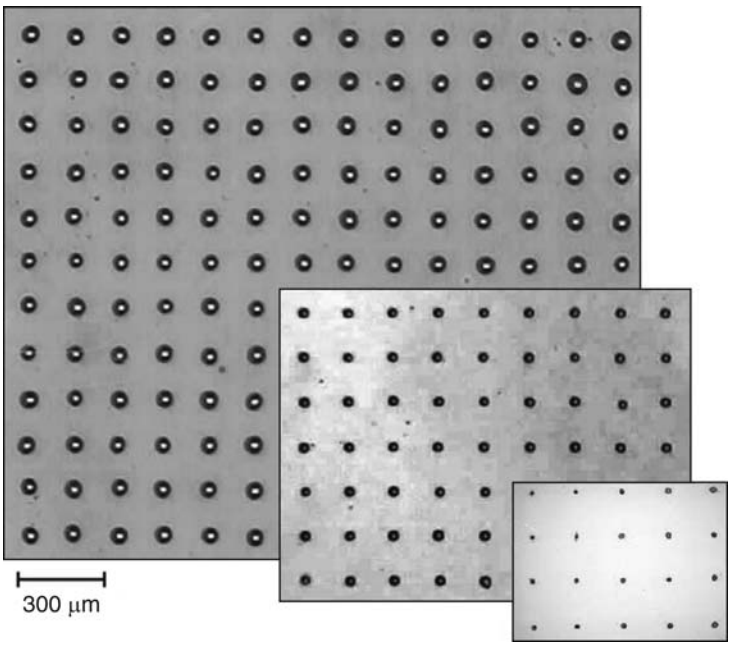

*Figure 6. Optical microscopy images of droplets from a 10 mg/ml solution of bovine serum albumin deposited onto a poly-*L*-lysine–treated glass substrate through laser direct-write addition (LDW+) printing. Different sizes correspond to different laser pulse energies and focusing conditions.*

of conductive silver ink is performed. The resulting embedded circuit occupies a footprint smaller than a single packaged LM555 chip. Figure 9 shows a photograph of the embedded blinker circuit. It is estimated that these LDW embedded circuits will occupy footprints of one-quarter or less than that of a printed circuit board design using prepackaged integrated circuits and require less than one-tenth the thickness. This shows that by using LDW processes, it is possible to fabricate functional electronic circuits buried within almost any surface, with the surface or substrate serving both as circuit board and packaging.

Conclusions

We have shown a variety of applications in which it is necessary to precisely locate and deposit sensitive materials that are easily damaged by other deposition techniques. LDW+ printing provides an ideal way to transfer chemically, physically, and biologically complex materials by allowing the laser interactions to affect only a localized region of the ink, thereby propelling the majority of the desired material to the receiving substrate without harm. This technique has been shown to transfer electrochemical materials such as

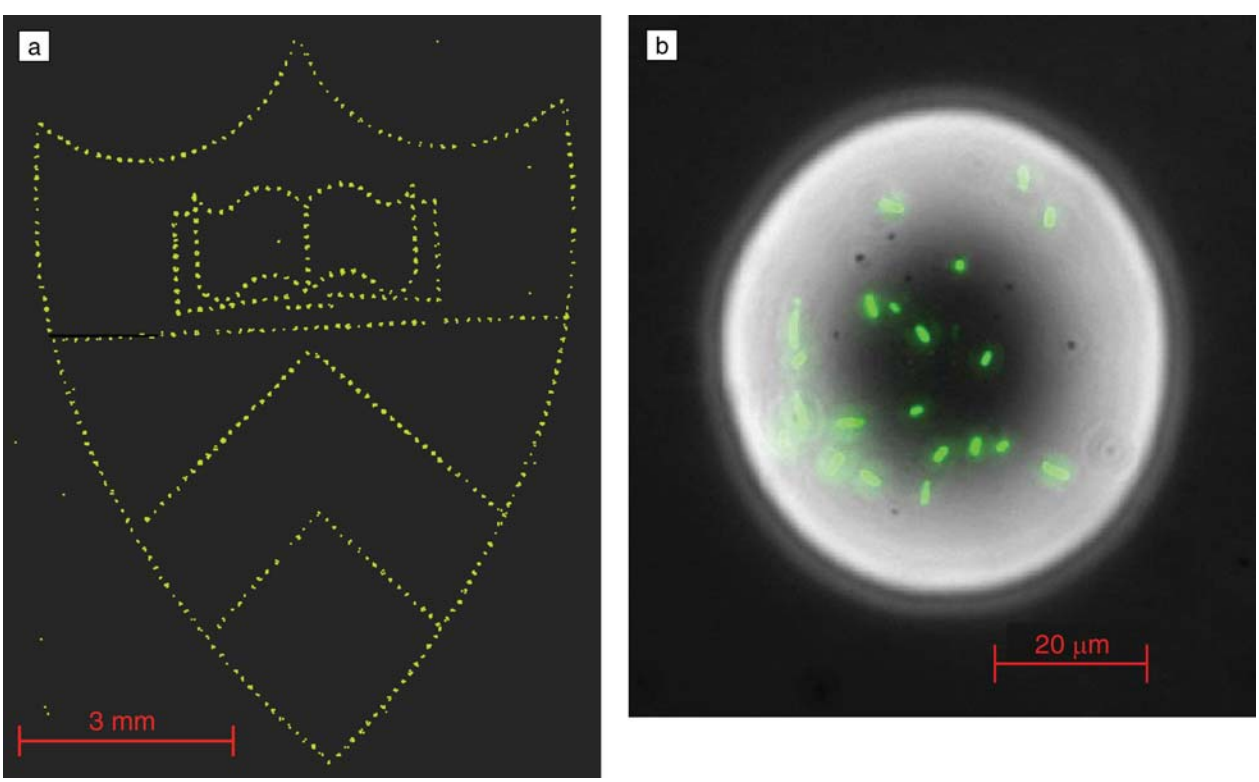

Figure 7. Laser direct-write addition (LDW+) printing of E. coli *bacteria on a glass slide. (a) Green fluorescence image indicating living cells that have been accurately placed to form a larger-scale structure (an outline of the Princeton University crest). (b) Close-up of an individual droplet. Each green spot corresponds to a single bacterium. (*E. coli *bacteria and fluorescent microscopy courtesy of R. Weiss, E. Adrianantoandro, and N. Kattamis of Princeton University.)*

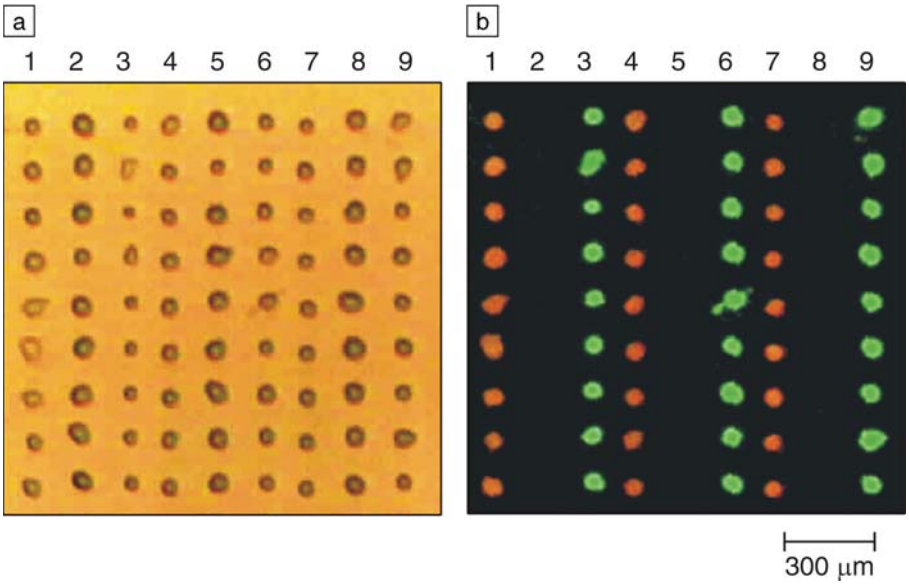

Figure 8. (a) Optical micrograph of a laser-printed DNA microarray. The array contains droplets of two DNA sequences corresponding to the human genes MAPK3 (columns 1, 4, and 7) and ETS2 (columns 3, 6, and 9), and droplets of a DNA-free solution (columns 2, 5, and 8). (b) Fluorescence image of the same microarray after hybridization with a solution containing Cy5-tagged complementary strands of the MAPK3 DNA (red emission signal), and Cy3-tagged complementary strands of the ETS2 DNA (green emission signal).

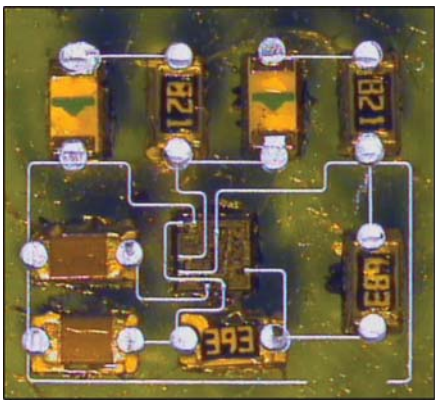

Figure 9. Laser direct-write addition (LDW+) printing of semiconductor bare dies and electronic components to fabricate a working blinker circuit embedded in a circuit board. The central square is an LMC555 die (1.4 mm × 1.4 mm) surrounded by surface-mounted resistors, capacitors, and light-emitting diodes. After transfer, the components are covered with polyimide. LDW– is then used to drill vias in the protective coating and LDW+ is used to deposit silver screen-printing ink in the vias to make electrical contact.

multicomponent, nanostructured oxides with high porosity while maintaining their electrochemical performance and physically porous structure. Vulnerable biomaterials such as proteins, DNA, bacteria, and stem cells can be deposited in a similar manner and remain viable after transfer. Finally, we have demonstrated that complete semiconductor circuits can be fabricated and embedded using a single LDW tool incorporating LDW+, LDW−, and LDWM. As the demand grows for high precision, conformal deposition, and controlled transfer of complex materials for advanced applications, LDW+ will continue to provide unique opportunities.

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References

1. J. Bohandy, B.F. Kim, and F.J. Adrian, *J. Appl. Phys.* **60** (1986) p. 1538.
2. F.J. Adrian, J. Bohandy, B.F. Kim, A.N. Jette, and P. Thompson, *J. Vac. Sci. Technol. B* **5** (1987) p. 1490.
3. J. Bohandy, B.F. Kim, F.J. Adrian, and A.N. Jette, *J. Appl. Phys.* **63** (1988) p. 1158.
4. V. Schultze and M. Wagner, *Appl. Surf. Sci.* **52** (1991) p. 303.
5. Z. Tóth, T. Szorenyi, and A.L. Tóth, *Appl. Surf. Sci.* **69** (1993) p. 317.
6. Z. Kántor, Z. Tóth, T. Szorenyi, and A.L. Tóth, *Appl. Phys. Lett.* **64** (1994) p. 3506.
7. I. Zergioti, S. Mailis, N.A. Vainos, P. Papakonstantinou, C. Kalpouzos, C.P. Grigoropoulos, and C. Fotakis, *Appl. Phys. A* **66** (1998) p. 579.
8. D.A. Willis and V. Grosu, *Appl. Phys. Lett.* **86** 244103 (2005).
9. J.A. Greer and T.E. Parker, *Proc. SPIE* **998** (1988) p. 113.
10. I. Zergioti, S. Malilis, N.A. Vainos, C. Fotakis, S. Chen, and C.P. Grigoropoulos, *Appl. Surf. Sci.* **127–129** (1998) p. 601.
11. E. Fogarassy, C. Fuchs, F. Kerherve, G. Hauchecorne, and J. Perriere, *J. Appl. Phys.* **66** (1989) p. 457.
12. W.A. Tolbert, I.-Y.S. Lee, M.M. Doxtader, E.W. Ellis, and D.D. Dlott, *J. Imaging. Sci. Tech.* **37** (1993) p. 411.
13. D.B. Chrisey, A. Piqué, R.A. McGill, J.S. Horowitz, B.R. Ringeisen, D.M. Bubb, and P.K. Wu, *Chem. Rev.* **103** (2003) p. 553.
14. P.K. Wu, B.R. Ringeisen, D.B. Krizman, C.G. Frondoza, M. Brooks, D.M. Bubb, R.C.Y. Auyueng, A. Piqué, B. Spargo, R.A. McGill, and D.B. Chrisey, *Rev. Sci. Inst.* **74** (2003) p. 2546.
15. S.M. Pimenov, G.A. Shafeev, A.A. Smolin, V.I. Konov, and B.K. Vodolaga, *Appl. Surf. Sci.* **86** (1995) p. 208.
16. 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** (1999) p. 279.
17. A. Piqué, A.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** (2000) p. 1872.
18. D.B. Chrisey, A. Piqué, J. Fitz-Gerald, R.C.Y. Auyeung, R.A. McGill, H.D. Wu, and M. Duignan, *Appl. Surf. Sci.* **154–155** (2000) p. 593.
19. A. Piqué, J. Fitz-Gerald, D.B. Chrisey, R.C.Y. Auyeung, H.D. Wu, S. Lakeou, and R.A. McGill, *Proc. SPIE* **3922** (2000) p. 105.
20. D. Young, R.C.Y. Auyeung, A. Piqué, D.B. Chrisey, and D.D. Dlott, *Appl. Phys. Lett.* **78** (2001) p. 3169.
21. C.B. Arnold, B. Pratap, A. Piqué, A.B. Geltmacher, and J.P. Thomas, *Proc. SPIE* **5339** (2004) p. 298.
22. R.C.Y. Auyeung, M.W. Nurnberger, D.J. Wentland, A. Piqué, C.B. Arnold, A.R. Abbott, and L.C. Schuette, *Proc. SPIE* **5339** (2004) p. 292.
23. C.B. Arnold, R.C. Wartena, B. Pratap, K.E. Swider-Lyons, and A. Piqué, *MRS Proc.* **689** (2002) p. 275.

24. B.R. Lewis, E.C. Kinzel, N.M. Laurendeau, R.P. Lucht, and X. Xu, *J. Appl. Phys.* **100** 033107 (2006).
25. C.B. Arnold, R.C. Wartena, K.E. Swider-Lyons, and A. Piqué, *J. Electrochem. Soc.* **150** (2003) p. A571.
26. C.B. Arnold, T. Sutto, H. Kim, and A. Piqué, *Laser Focus World* **40** (2004) p. 9.
27. H. Kim, G. Kushto, C.B. Arnold, Z.H. Kafafi, and A. Piqué, *Appl. Phys. Lett.* **85** (2004) p. 464.
28. D. Linden and T.B. Reddy, eds. *Handbook of Batteries, 3rd ed.* (McGraw-Hill, New York, 2001).
29. C.B. Arnold, A. Piqué, R. Auyeung, and M. Nurnburger, "Laser-based technique for producing and embedding electrochemical cells and electronic components directly into circuit board materials," U.S. Patent 6,986,199 (January 17, 2006).
30. D.A. McKeown, P.L. Hagans, L.P.L. Carette, A.E. Russell, K.E. Swider, and D.R. Rolison, *J. Chem. Phys. B* **103** (1999) p. 4825.
31. A. Piqué, C.B. Arnold, H. Kim, M. Ollinger, and T.E. Sutto, *Appl. Phys. A* **79** (2004) p. 783.
32. C.B. Arnold, H. Kim, and A. Piqué, *Appl. Phys. A* **79** (2004) p. 417.
33. R.C. Wartena, A.E. Curtright, C.B. Arnold, A. Piqué, and K.E. Swider-Lyons, *J. Power Sources* **126** (2004) p. 193.
34. M. Ollinger, H. Kim, T.E. Sutto, F. Martin, and A. Piqué, *J. Laser Micro. Nanofab.* **1** (2006) p. 102.
35. T.E. Sutto, M. Ollinger, H. Kim, C.B. Arnold, and A. Piqué, *Electrochem. Solid-State Lett.* **9** (2006) p. A69.
36. M. Colina, M. Duocastella, J.M. Fernández-Pradas, P. Serra, and J.L. Morenza, *J. Appl. Phys.* **99** 084909 (2006).
37. D.J. Odde and M.J. Renn, *Biotechnol. Bioeng.* **67** (2000) p. 312.
38. J.A. Barron, P. Wu, H. Ladouceur, and B.R. Ringeisen, *Biomed. Microdevices* **6** (2004) p. 139.
39. B. Hopp, T. Smausz, N. Kresz, N. Barna, Z. Bor, L. Kolozsvári, D.B. Chrisey, A. Szabó, and A. Nógrádi, *Tissue Eng.* **11** (2005) p. 1181.
40. A. Doraiswamy, R.J. Narayan, T. Lippert, L. Urech, A. Wokaun, M. Nagel, B. Hopp, M. Dinescu, R. Modi, R.C.Y. Auyeung, and D.B. Chrisey, *Appl. Surf. Sci.* **252** (2006) p. 4743.
41. B.R. Ringeisen, P.K. Wu, H. Kim, A. Piqué, R.Y.C. Auyeung, H.D. Young, and D.B. Chrisey, *Biotechnol. Progr.* **18** (2002) p. 1126.
42. P. Serra, J.M. Fernández-Pradas, F.X. Berthet, M. Colina, J. Elvira, and J.L. Morenza, *Appl. Phys. A* **79** (2004) p. 949.
43. J.A. Barron, H.D. Young, D.D. Dlott, M.M. Darfler, D.B. Krizman, and B.R. Ringeisen, *Proteomics* **5** (2005) p. 4138.
44. J.M. Fernández-Pradas, M. Colina, P. Serra, J. Domínguez, and J.L. Morenza, *Thin Solid Films* **453–454** (2004) p. 27.
45. B.R. Ringeisen, D.B. Chrisey, A. Piqué, H.D. Young, R. Modi, M. Bucaro, J. Jones-Meehan, and B.J. Spargo, *Biomaterials* **23** (2002) p. 161.
46. J.A. Barron, D.B. Krizman, and B.R. Ringeisen, *Ann. Biomed. Eng.* **33** (2005) p. 121.
47. Thanks to R. Weiss and E. Adrianantoandro from Princeton University for providing *E. coli* bacteria and fluorescent imaging of patterns.
48. P. Serra, M. Colina, J.M. Fernández-Pradas, L. Sevilla, and J.L. Morenza, *Appl. Phys. Lett.* **85** (2004) p. 1639.
49. M. Colina, P. Serra, J.M. Fernández-Pradas, L. Sevilla, and J.L. Morenza, *Biosens. Bioelectron.* **20** (2005) p. 1638.
50. A.S. Holmes and S.M. Saidam, *J. Microelectromech. Sys.* **7** (1998) p. 416.
51. A.S. Holmes, *Proc. SPIE* **4426** (2002) p. 203.
52. A. Piqué, B. Pratap, S.A. Mathews, B.J. Karns, R.C. Auyeung, M. Kasser, M. Ollinger, H. Kim, S. Lakeou, and C.B. Arnold, *Proc. SPIE* **5713** (2005) p. 223.
53. A. Piqué, S.A. Mathews, R.C. Auyeung, M. Ollinger, H. Kim, B. Pratap, C.B. Arnold, and T.E. Sutto, *Proc. SPIE* **5662** (2004) p. 564.
54. A. Piqué, S.A. Mathews, B. Pratap, R.C.Y. Auyeung, B.J. Karns, and S. Lakeou, *J. Microelectron. Eng.* **83** (2006) p. 2527. □