Using Laser-Induced Thermal Voxels to Pattern Diverse Materials at the Solid–Liquid Interface

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Supporting Information

ABSTRACT: We describe a high-resolution patterning approach that combines the spatial control inherent to laser direct writing with the versatility of benchtop chemical synthesis. By taking advantage of the steep thermal gradient that occurs while laser heating a metal edge in contact with solution, diverse materials comprising transition metals are patterned with feature size resolution nearing 1 μm. We demonstrate fabrication of reduced metallic nickel in one step and examine electrical properties and air stability through direct-write integration onto a device platform. This strategy expands the chemistries and materials that can be used in combination with laser direct writing.

KEYWORDS: laser direct write, laser-induced heating, Ni electrode, solvothermal synthesis, metals, microstructures

Revolutionary scientific and technological advances are often driven by the development of processing approaches that provide integration of diverse materials into synergistic systems via precise chemical and spatial control. For example, photolithography serves as the foundational process for the production and increasing complexity of integrated circuits by enabling nanoscale patterning of layered thin films and features. Yet, as the miniaturization of products and processes advances along with the next generation of flexible and nonplanar devices, the continued development of rapid and deployable prototyping techniques that offer high precision, resolution, and broad customizability of materials—from polymers to ceramics, metals and alloys—is of critical importance.

Specifically, the ability to deposit electronic materials such as metals and oxides using laser direct write approaches offers flexibility for patterning on diverse substrates as well as faster optimization times and lower operating costs for device prototyping as compared to clean-room lithographic procedures. In particular, fine-feature patterning of metals and metal oxides is increasingly addressed using laser direct write (LDW) techniques1,2 that enable deposition of higher resolution features as compared to, for example, inkjet methods.3 Notable examples include selective laser sintering and laser-induced forward transfer (LIFT),4 which are used to deposit metals and oxides. For sintering techniques, a nanoparticle ink or powder is first formulated and deposited before laser-annealing on a surface.5,6 In LIFT, the target material must be synthesized and coated with the appropriate level of adhesion onto a donor substrate.4 In both methods, the material synthesis and patterning are carried out separately. Another direct-write approach, focused electron beam induced deposition (FEBID),
has been shown to print metals and alloys with nanoscale resolution, but requires high vacuum conditions as well as specialized instrumentation and chemical precursors.\textsuperscript{7,8}

Approaches that combine the spatial control of laser deposition with in situ metal, metalloid, or metal oxide synthesis directly from a precursor liquid phase at ambient conditions could be advantageous in terms of promoting homogeneity, ease of handling, and, in principle, more highly tunable chemistries.\textsuperscript{9} However, current methods have been primarily limited to photoreduction of metal ions in solution or decomposition of select, highly reactive and toxic precursor gases. Examples include deposition of iron from gas-phase decomposition of iron pentacarbonyl,\textsuperscript{10} silicon and germanium nanowires from decomposition of silane and germane gases,\textsuperscript{11,12} silver and gold via photoreduction of the metal salt solutions,\textsuperscript{13,14} and platinum and palladium from aqueous solution via the use of an iron oxalate photosensitizing agent.\textsuperscript{15} Patterned growth of zinc oxide and iron oxide crystals has been achieved using laser-assisted hydrothermal growth conditions.\textsuperscript{16−18} Unfortunately, photoreductive approaches are not easily translatable to many metals or oxides given the wide range of reduction and oxidation potentials across, for instance, the transition metals and the limited availability of suitable photoactivatable reducing agents. New laser processing strategies which provide for in situ synthesis and deposition of a broader range of materials from liquid precursors would facilitate the progress of high-resolution, laser-driven manufacturing.

Here, we present a direct-write fabrication strategy that combines the spatial control inherent to LDW approaches with the flexible and versatile chemistry of benchtop chemical synthesis, enabling patterning and integration of a far wider range of metal and metal oxide materials than previously demonstrated. We surmised that if conditions of high temperature could be generated within a laser-defined reaction volume (voxel) at the laser’s focal point, then we could use these conditions for hydrothermal or solvothermal-like syntheses of materials from a surrounding liquid precursor solution. Previous analysis of pulsed laser ablation of metal targets submerged in liquid reveals that, in the presence of an optical absorber, a hot zone or plasma plume can be generated at the focal point that reaches temperatures on the order of several thousand degrees.\textsuperscript{19} Additionally, LDW of copper from solution has been investigated using high intensity visible laser light sources (e.g., Ar$^+$ 488 nm laser,\textsuperscript{20} 532 nm Q-switch Nd:YAG\textsuperscript{21}) focusing into absorbing metal salt solutions to achieve a laser-induced reaction zone\textsuperscript{22} (we refer to it here as a laser-induced thermal voxel; LITV). Indeed, here we show that generation and spatial translation of these LITVs generated at an absorbing edge (using near-infrared CW laser light) provides a general route for direct writing of a wide range of metals and oxides, greatly expanding the chemistries and materials that can be used in combination with laser direct writing techniques.

The fabrication procedure that we used to direct-write materials using LITVs is illustrated in Figure 1a. Key to this process is that both the initiation and propagation of deposition require the localized optical absorption of the laser light and subsequent heating of a precursor solution. Examples of suitable optical absorbers include nanoparticles (either in solution or on the surface, such as in silver paint), a strongly absorbing precursor liquid or thin film,\textsuperscript{16} as well as the edge of an absorbing layer (e.g., a metal layer). For example, as shown in Figure 1b, the absorber is a platinum film on a glass substrate that was deposited via laser direct writing using photoreductive chemistry as described previously.\textsuperscript{15} Next, the substrate is rinsed in a solution containing the metal or metal oxide precursor, in this case, Ni(NO$_3$)$_2$ dissolved in water. When we irradiate the edge of the platinum film with a tightly focused continuous wave laser (operating at 750 nm and focused to $\sim 1$ mm diameter spot using a 1.3 numerical aperture microscope objective), high temperatures reached at the focal point allow for localized deposition of nickel oxide. Often a bright, broadband region is observed at the laser focus (Figure 1b), which presumably is the LITV-generated hot zone.\textsuperscript{19} Translation of either the substrate or the laser beam from the edge of the nascent structure enables formation of arbitrary two-dimensional patterns, where the deposited nickel oxide now serves as the optical absorber and enables propagation of the writing process. Increasing the laser input power results in increased width of resultant NiO lines and tends to increase the roughness of surfaces exposed to the liquid as shown in Figure S1.

To better understand the physical nature of this reaction volume, we used the two-dimensional steady-state heat equation (Laplace Equation) to model the temperature gradients near the liquid/metal interface. Figure 1c shows the laser (heat) source positioned near the interface and associated temperature distribution. We modeled the metal and glass as
identical two-dimensional rectangular slabs with lengths of 10 μm and widths of 20 μm. The laser source, which is modeled as a 1 μm diameter semicircle, is placed with its center directly at the liquid/metal interface; we assume a steady state temperature rise at laser spot of ~2000 K (see the experimental details in the Supporting Information) and treat the liquid as a nonabsorbing medium—a valid assumption for many precursors given our laser wavelength (750 nm). Using the laser-induced temperature rise as a boundary condition, we discretized the Laplace Equation over these two rectangular domains using a 10 nm square mesh and solved for the temperature distribution using a central-difference scheme. For the calculations shown in Figure 1c, we assumed thermal conductivities for the metal (assumed as Pt) and liquid water at standard temperature and pressure taken from literature.23 We assumed semi-infinite boundary conditions in all directions except for the liquid/metal boundary. At this interface, the conductive heat flux of the metal and liquid are equal to the heat transport across the metal/liquid boundary, so the interface is subjected to the following boundary conditions

\[ -\kappa_{\text{metal}} \frac{\partial T_{\text{metal}}}{\partial x} = \frac{T_{\text{metal}} - T_{\text{liquid}}}{R_{\text{int}}} \]

and

\[ -\kappa_{\text{liquid}} \frac{\partial T_{\text{liquid}}}{\partial x} = \frac{T_{\text{metal}} - T_{\text{liquid}}}{R_{\text{int}}} \]

where \( k \) is the thermal conductivity, \( T \) is the temperature (which is a function of both \( x \), the length of the slab and direction normal to the interface, and \( y \), the width of the slabs), and \( R_{\text{int}} \) is the resistance across the metal/liquid interface. This resistance, often referred to as the thermal boundary resistance or Kapitza resistance,24,25 relates the heat flow across the interface to the finite temperature drop at this boundary, taking into account both the conduction and convection heat transfer mechanisms (i.e., all pertinent nanoscopic heat transport mechanisms) from the metal into the surrounding liquid at the solid/liquid boundary. A dominant resistance in nanosystems, this resistance has been extensively studied in the past decade.26 On the basis of previous reports, we assume a thermal boundary resistance of 2 × 10^{-8} m² W^{-1}. This thermal boundary resistance will dictate how severe the thermal gradient at the metal/liquid interface will be, a key factor in understanding the buildup of energy leading to a laser-induced hot zone at the metal edge. Such a sharp temperature gradient produces violent boiling at the reaction zone and can also lead to pinning of gas bubbles at the substrate in front of the leading edge of the structure, interfering with subsequent fabrication (Figure S2). However, pinning is easily mitigated by increasing the wettability of the substrate (e.g., plasma cleaning).

Applying this LITV approach, a range of metals and metal oxides can be patterned in desired shapes and proximities. Figure 2 shows deposition of 13 diverse metals and metal oxides according to the position of the metallic element within the periodic table demonstrating site-selective patterning of a wide array of materials with microscale precision. Using a digital mask-directed laser scanning approach,27 each material could be positioned with high accuracy, as is shown in the energy-dispersive X-ray spectroscopy (EDS) composite map in Figure 2c, as well as in specific patterns (Figure 2e, f). The individual element EDS maps are shown in Figure S3.

Although most of the materials in Figure 2 were deposited by using the edge of a neighboring material as the initial optical absorber (as demonstrated in Figure 1), we found that a number of precursor solutions could also be used directly without the need for an additional absorber. Ruthenium, for example, deposits directly from a solution of ammonium hexachlororuthenate(IV) because of the relatively high absorbance of the precursor by the fundamental wavelength used here (750 nm, Figure S4). Ferric oxide could also be patterned directly from potassium ferrate aqueous solution which we attribute to the in situ formation of nanoparticles produced as the potassium ferrate decomposes following initial hydration (Figure 2f). The EDS map of oxygen (Figure 2d) indicates that, as expected, while the noble metals (Ir, Ru, Rh, Pd, Pt) show no oxidation, the base metals (V, Cr, Mn, Fe, Co, Ni, Cu, and Mo) display some degree of oxidation. We note that, at present, initial deposition of the base metals can result in mixed oxide phases as is observed for iron oxide structures using different precursors (Figure S5). In principle, such materials may be reduced from oxides to metals in subsequent processing steps using high-temperature chemical reduction procedures (e.g., using forming gas); however, it would be
significantly enabling to be able to pattern, for example, abundant (nonprecious) reduced metals (e.g., copper, nickel) in a single step using the LITV process.

To begin to address this challenge, we focused on the direct writing of Ni given its resistance to corrosion and potential use in a wide variety of devices (e.g., batteries, supercapacitors, thermocouples, specialty alloys). As indicated in Figure 1, LITV fabrication from Ni(NO$_3$)$_2$ dissolved in water yields oxidized nickel. XRD analysis indicated materials deposited in this manner are comprised of crystalline NiO (Figure 3a) which

decades$^{28}$ and has also been used for LDW of copper using copper oxide nanoparticle precursors and nanowires.$^{29,30}$ A general polyol reduction reaction proceeds as such

$$2\text{HO(CH}_2)_2\text{OH} \xrightarrow{\text{Δ(heat)} - 2\text{H}_2\text{O}} \text{C}_2\text{H}_4\text{O}_2$$

Here, ethylene glycol is thermally dehydrated via laser-induced, photothermal heating to yield acetaldehyde ($\text{C}_2\text{H}_4\text{O}_2$) that can subsequently reduce Ni$^{2+}$ to Ni with diacetyl ($\text{C}_4\text{H}_6\text{O}_2$) as the primary oxidation product. Subsequent photothermal interaction of the metal can facilitate agglomeration and sintering$^{29}$ and potentially increase the rate of the reduction process via photochemical excitation.$^{30}$ SEM images indicate a high surface area, macroporous morphology of deposited Ni materials (Figure 3b) with a minimum line width nearing 1 μm fabricated at a rate of 1 mm s$^{-1}$ (Figure S6). The resultant silvery-white materials are shown in the optical reflectance images of mesh structures fabricated in this manner (Figure 3c, d). Here, we fabricated grid structures with relatively large (∼10 μm) and small (∼1.5 μm) pore mesh sizes, as such structures have applications for current collection$^{31}$ and electromagnetic shielding.$^{32}$

In order to measure the electrical properties of the Ni metal, we connected a series of gold electrodes with a Ni wire deposited with the LITV technique. As shown in Figure 4a, the electrodes were wire-bonded to a standard chip carrier and 4-point resistance measurements were taken between three sets of four neighboring electrodes. The measured resistivity ($\rho$) of 1.3 × 10$^{-5}$ Ω m, for ease of estimation, assumes a fully dense wire with cross sectional area 8 μm$^2$ by 2 μm ($\rho$ for bulk Ni = 1 × 10$^{-8}$ Ω m). Figure 4c illustrates the uniformity of resistance along the wire shown in Figure 4a, b and, importantly, this material displayed good long-term electrical stability in air (Figure 4d). Overall, the ability to write a functional, oxidation-prone metal directly from solution (i.e., no precursor nanoparticle ink) offers a flexible pathway forward for the deposition of diverse metals and, in principle, metal alloys (Figure S7).

We have developed a methodology for optically driven, direct writing of a wide range of metals and metal oxides at the ∼1 μm scale. Given the vast variable space through which this system can be potentially manipulated (e.g., variation in solvent, precursor chemicals, laser power, wavelength, pulse parameters), we expect that a far broader range of materials, chemistries, and morphologies with increased resolution are possible, far beyond the few examples demonstrated here. Unlike laser sintering of powder, decomposition of gaseous precursors, or nanoparticle ink printing, we have shown that many metal and oxide materials can be directly synthesized and patterned in situ via locally generated thermal voxels in solutions under ambient conditions. By employing the highly customizable and variable chemistries available using solution-based reaction conditions, this process may dramatically simplify mixed material manufacturing (sequential deposition followed by simple rinsing or integration with high throughput microfluidics), reduce cost (inexpensive and readily available precursors with no need for high vacuum conditions), and ultimately expand the breadth of materials compatible with LDW additive manufacturing technology.

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Figure 4. Resistivity and long-term stability of Ni materials. (a) To measure resistivity, we wrote a Ni wire to connect a series of gold pads, subsequently wire-bonded them, and took 4-point resistance measurements between the sets of neighboring electrodes. Scale = 0.5 mm. (b) Magnified (left) and cross-section (right) SEMs are shown in panel b, scales = 5 μm. (c) Measured resistance of the nickel wire versus wire length. The numbers in parentheses indicate the resistance measured between corresponding electrodes shown in (a). (d) The resistance between contacts connected by Ni wires in a device similar to that shown in panel a was measured immediately after fabrication (R0) and over time after aging in open air (Rt). Each time point represents the average of 9 measurements and shows device stability following an initial increase in resistance between contacts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b06625.

Detailed experimental procedures of the precursors, laser setup, and thermal modeling as well as and Figures S1–S7 (PDF)

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■ REFERENCES


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