

Supplementary Material

Substrate thermal conductivity controls ability to manufacture microstructures via laser-induced direct write

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SAMPLE PREPARATION

Ionic Precursor

To prepare the silver nitrate (AgNO_3) solutions used in this work, we dissolve 250 mg of solid AgNO_3 in 2 mL of DI water. Separately, 400 mg of polyvinylpyrrolidone (40,000 MW) is mixed in 10 mL of ethanol. Each solution is then individually mixed and sonicated for five minutes. Following this, the PVP solution is combined with the AgNO_3 solution; we further sonicate this mixture for 30 minutes.

To avoid premature photo-decomposition of our AgNO_3 , all preparation is performed in the dark. Additionally, the solution is wrapped in foil following sonication and, for long-term storage, placed in a light-free container. We find that our AgNO_3 precursor is apt for direct write, at the minimum, at least one week following this preparation; we have not attempted synthesis on solutions stored longer than this duration.

Substrate

Although many previous works regarding the additive manufacturing of Ag microstructures have relied on a silane adhesion layer on the substrate prior to deposition of the metal, we find this is not necessary for laser thermal direct write of such structures; all results in this work are on ‘bare’ substrates that have been only alcohol cleaned. We regard this minimized sample preparation as a benefit to the potential for rapid-prototyping with this method. Nonetheless, our preliminary studies considered the use of a silane layer as well as plasma cleaning of the substrate. We find neither are necessary for our method and simply increase preparation time; we did not find ill-effects associated with either.

In the case of plasma-cleaned surfaces, we O_2 plasma clean the substrate for 30 minutes prior to deposition of Ag structures. Similarly, when considering silane-coated substrates, we plasma-clean prior to silane deposition. Following plasma-cleaning, we spin-coat trimethoxysilane at 3500 RPM and then bake the sample for one hour at 400 K.

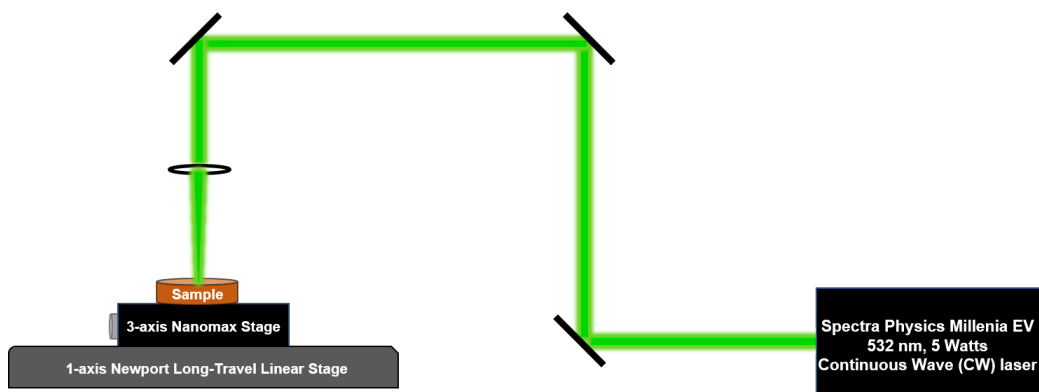


Figure S1. Experimental setup for our laser thermal direct write of Ag microstructures. In the case of our high-repetition, femtosecond measurements, the continuous wave laser is replaced with a Spectra Physics Spirit laser.

EXPERIMENTAL SETUP

A schematic of our experimental setup can be seen in Fig. S1. The primary laser used in this work is the 532 nm, continuous-wave beam output from a Spectra Physics 5 W Millenia EV laser source. This output is directed through a periscope lens array, microscope objective/focal lens, passes through the liquid layer overlying the sample, and then focused on to the sample surface at the substrate/liquid interface. As described in detail in the primary manuscript, the temperature rise associated with the laser interaction at this interface leads to thermal decomposition of the overlying ionic liquid precursor, allowing for formation and thus deposition of metallic microstructures. The referenced substrates are submerged beneath 2 mm of the ionic precursor, placed in the ‘Sample’ in the shown schematic.

We do not form structures via beam motion, due to alterations in spot size and beam quality, but instead move the substrate/liquid holder. To do so, we have two translation stages, allowing for 3D movement for easy focusing of the beam on the substrate surface, well-defined/high-resolution movements on the microscale, as well as rapid movements for investigation to scan-speeds. For the rapid scan speeds, we use a linear motorized stage from Newport, with movement velocities from 0-25 mm s⁻¹. Mounted on top of this linear stage is a Thorlabs Nanomax stage, allowing for movements from 0-2.5 mm s⁻¹, yet with slightly better step-resolution.

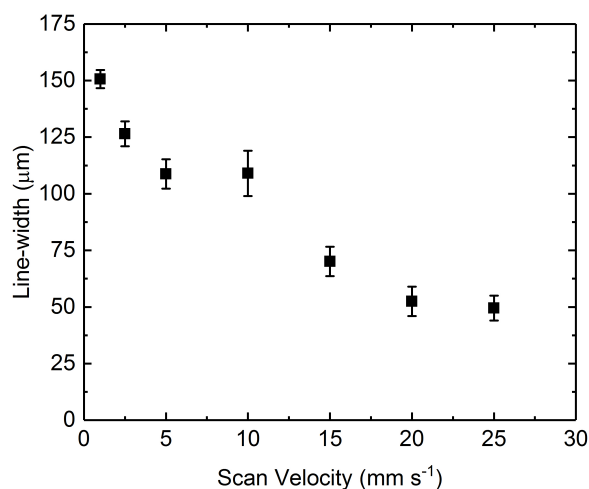


Figure S2. Measured line width as a function of sample scan velocity using a 532 nm, continuous wave laser at 2 W.

SCAN VELOCITY MEASUREMENTS

As mentioned previously, the results in the manuscript are at a constant scan velocity of 2.5 mm s⁻¹, yet, the temperature increase predicted via Equation 1 in the primary manuscript implies a dependence on the velocity associated with the direct write process. Thus, to further reinforce the dependence on thermal accumulation and the steady-state temperature rise on microstructures formed by laser direct write, we vary the scan velocity from 0.5 to 25 mm s⁻¹. As seen in Fig. S2, the width of the microstructures are greatly affected by the rate of sample motion, and exponentially plateau off to a nearly constant width at increased speeds. Given such, this is another parameter that must be considered during laser direct write processing to optimize the manufacturing quality.

CHARACTERIZATION

SEM

Scanning electron micrographs are obtained using a Zeiss 982 field emission SEM in both secondary electron detection and using an in-lens detection setup. The micrographs shown in the manuscript are obtained with secondary electron detection, but our analysis utilized both setups.

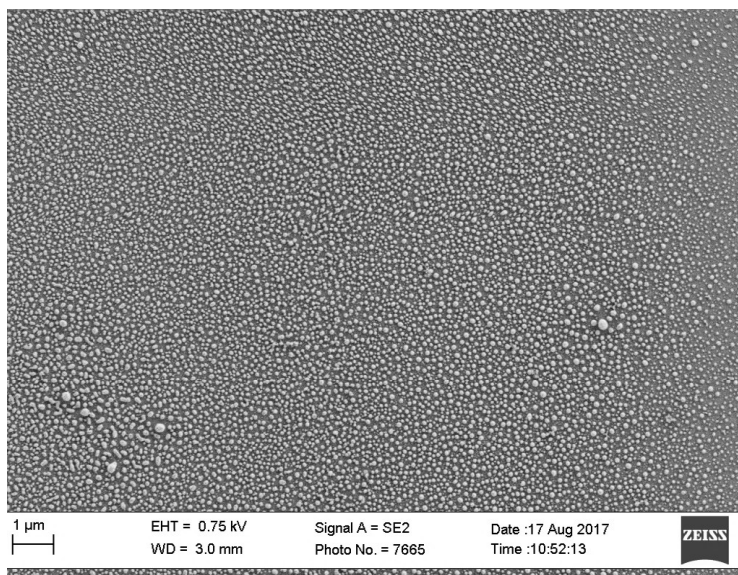


Figure S3. High magnification SEM micrograph of the center of a silver microstructure formed on a crystalline quartz substrate. As seen, particle formation occurs on the top of the structure due to the steady-state temperature rise associated with the laser interaction at the solid-liquid interface.

From the micrographs, we use ImageJ, open-source software to measure the width, height, and lengths of the structures that are referenced in the primary manuscript.

As discussed in the manuscript, we hypothesize the role of the steady-state temperature rise during laser interactions at a solid-liquid interface to be a primary factor in the deposition of metallic structures via laser direct write. In such, we discuss the various mechanisms of which decomposition can occur (i.e., nucleation and growth of the formed Ag from thermal decomposition of the silver nitrate). This notion is reinforced by the qualitative assessment of the obtained SEM micrographs. As seen in Fig. S3, which is a zoomed-portion of the primary structure, particle formation occurs within the formed silver microstructures. Additionally, we find at large dwell times, such as continuous irradiation for numerous seconds, that the structures have a much larger height than those at our scan velocity of 2.5 mm s^{-1} , as determined via our SEM micrographs

Profilometry

Due to the structure size and width, profilometry provides an accurate measure of line-width and relative roughness across the microstructure without the need for atomic force microscopy. We perform line scans across the width of the synthesized microstructures for comparison to the

line-widths measured via SEM. We find that the two methods are in good agreement and provide similar values.

XRF

To confirm the microstructures are truly Ag, we perform x-ray fluorescence (XRF) measurements of the produced microstructures. As expected, the only element detected, other than gaseous species due to atmospheric interactions, is silver. Of course, one would expect additional oxygen, if it could be accurately measured, due to oxidation of the Ag structures due to exposure to atmosphere.