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Localized Physical Vapor Deposition via Focused Laser Spike Dewetting of Gold Thin Films for Nanoscale Patterning

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ABSTRACT:

Focused laser spike (FLaSk) excitation has been demonstrated as a reliable technique for the patterning of micro-to-nanoscale features locally by thermocapillary shear of thin films. Recent work on polymer thin films has revealed that overlapping laser scans can leverage coupled thermal and fluid effects to create subwavelength patterns. Compared to polymeric films, metallic thin films possess both a lower melt viscosity and higher surface tension. Here we investigate overlapping effects in the dewetting of ~15 nm gold thin films on borosilicate and quartz glass substrates with a 532 nm continuous wave laser. During this process, FLaSk initiates capillary and thermocapillary dewetting simultaneously. Further, the low oxidation potential and high vapor
pressure of gold lead to non-equilibrium vaporization during heating. Since the parameters of overlapping scans control the amount of material that is heated and to what temperature it is heated, selection of laser power, scanning distance, writing speed, and numerical aperture results in particles with different sizes and spacing deposited on the writing substrates or a positioned superstrate through a laser-induced localized physical vapor deposition (LILPVD) process. If the laser parameters are selected within a specific working range, uniform or periodic particle distributions can be repeatably deposited in this fashion, which can then be used as seeds for nanomaterial growth. In addition, if the substrate melts during FLaSk, the viscous forces of the liquid-on-liquid dewetting broadens the range of patterning conditions by resisting the motion of the gold leading to more uniform particles over a large range of parameters.

KEYWORDS: Physical vapor deposition, focused laser, dewetting, gold, thin film, nanoparticles

Thermal excitation, a natural thermodynamic variable, is a ubiquitous driving force and thus is applicable to any materials system. Laser spike annealing (LSA), which employs photothermal excitation to provide tunable localized rapid heating and cooling conditions, has been studied as patterning and metrology method for the polymeric, semiconductor, and metallic systems.\textsuperscript{1-7} The conjugate forces of thermal gradients can also be utilized as a means of directing soft matter. Thermocapillarity is one of the most studied coupled forces for patterning. Thermocapillary shear is described by the thermal Marangoni coefficient, $\beta = \delta \gamma / \delta T$ (where $\gamma$ is the free-surface tension of the material). The Marangoni coefficient, in turn, determines the thermocapillary Marangoni shear, $\tau = \beta \nabla T$.\textsuperscript{8} As $\beta$ is generally negative, these forces have previously been generated electrically or optically to drive soft matter down thermal gradients, as we have recently reviewed
in the context of polymeric patterning. In the 1990s, Tam, Grigoropoulos and colleagues were the first to utilize thermocapillary dewetting towards the deliberate generation of structures by employing a focused laser beam to create such structures for magnetic memory. In this work, the melt pool generated by a focused laser spike (FLaSk) on a steel alloy provided both the mobility and the driving force to locally dewet a ring of raised metal around a local depression. On further FLaSk heat treatment, through coupled solvocapillary effects of concentration shifts in the alloy, a central region of increased height to act as an isolated “bit” structure. This early work illustrated the key advantage of FLaSk dewetting and other thermocapillary approaches—namely, thermal gradients simultaneously provide both the mobility and driving force for assembly. Further, thermal gradients can be independently tuned from the peak temperature by shrinking the heat source, allowing for thermal gradients $10^4$ to $10^9$ K/m be created from temperature differences from 10 to 1000 K. The reduced peak temperature allows thermocapillary approaches to avoid thermal degradation mechanisms. In this way, subsequent thermocapillary work has demonstrated the dewetting of semiconductors, polymers, small molecules, liquid crystals, and metallic thin films.

Our work has heretofore investigated the application of FLaSk dewetting to polymer thin films and more recently, the consecutive dewetting of polymer-metal bilayers. The results of this work revealed several characteristic behaviors of the dewetting process: (1) the shear generated during dewetting is sufficient to drive the alignment of mesostructured phases such as block copolymer (BCP) microdomains; (2) the morphology of dewetted trench-ridge structures in polymer thin films heated by photothermal excitation of the supporting substrate through the polymer film is self-similar during development and depends only on (a) the initial film thickness
(due to anti-reflection coating (ARC) effects) and (b) the polymer molecular weight, which determines the melt viscosity of the system;\(^2\) (3) Bilayer mobility, such as that imparted by same-species brush layers or two stacked polymers, can lead to shifts in power response and split into segmented patterns,\(^3\) which have since been shown by Elashnikov \textit{et al.} to also arise in high-speed FLaSk dewetting;\(^2\) and (4) the material is \textit{moved} rather than \textit{removed}, so overlapped writing can lead to subwavelength patterning independent of the thermal spot size.\(^2\) Therefore, as a means of polymer lithography, FLaSk dewetting possesses the advantages of being non-contact, subwavelength, developer and photochemical-free, and applicable to a wide array of materials.

When naïvely compared to polymer melts, metallic melts can be viewed as polymers of molecular weight (MW) approaching 0. As such, the morphologies observed during large-area pulsed laser dewetting tend to rapidly form into islands.\(^2\) In addition, metals tend to have high surface tensions. This is readily apparent in Ferrer \textit{et al.}'s examination of FLaSk heating of microdroplets and microfilms of metals, specifically bismuth and tin.\(^2\) In this work, it was observed that microdroplets, when heated with at \(\sim 33\) μm laser spot, retract into conventional wetting-determined semispherical shapes, but, in contrast, microfilms, would dewet into trench-ridge structures similar to the thermocapillary features in polymers and metal monoliths. This was also observed by Briere \textit{et al.} in early work on laser curing of gold inks.\(^2\) In that study, an undesirable “bowl” shape that formed in the center of the cured nanoparticle ink line was attributed to thermocapillary dewetting. This “pull” and “push” mode illustrates the competition of the capillary and thermocapillary effects (Figure 1a and Figure S1). However, although considerable research has been conducted on laser and non-laser dewetting of metal thin films,\(^30-34\) this competitive regime has not been explored in a systematic way, nor have the effects of overlapping
patterning been considered. An additional consideration of processes with molecular melts, such as metals, is that they possess much higher vapor pressures than polymeric systems. This property is often utilized for the formation of nanoparticles or thin films of metals through physical vapor deposition (PVD), where a target substrate is held above or placed downstream of a crucible filled with molten metal or monomer to collect deposited nanoparticles. Such processing can be conducted in vacuum or flowing gas to inhibit oxidation and allow for large thermal gradients between the source and target. In FLaSk, the latter effect can even occur in ambient conditions. In a related technique, Shou et al. recently used a laser with a spot size of 60–70 μm to induce the evaporation of zinc from a microns-thick nanoparticle film in ambient conditions to deposit high-crystallinity zinc on a proximate flexible superstrate. This allowed for the rapid fabrication of zinc-based microcircuits.

The current work explores how the dewetting of gold nanofilms exposed to microscale/sub-microscale FLaSk compares to polymeric systems and past metallic film results, with particular interest in overlapping line writing. With thinner films and smaller laser spots, both the capillary and thermocapillary effects are enhanced. Additionally, through selection of substrates with melting temperature above and below that of the metal film, bilayer mobility effects are evaluated. At the correct tuning of film and substrate mobility, overlapped writing effects can lead to simultaneous dewetting and PVD in the dewetted region. The nanoparticles created by this process can be tuned in size through the laser parameters, with sharper thermal gradients leading to smaller particles, and can result in dense arrays of sub-100 nm particles in large areas. A clear change of the color indicates the localized surface plasmon resonance (LSPR) induced by different size of gold nanoparticles. By placing another acceptor superstrate above the annealed film at a
distance of tens of microns, the generated particles are collected on the superstrate acceptor. This process, laser-induced local PVD (LILPVD), increases the capabilities of FLaSk dewetting to include transfer printing. As a rapid, mask-free, ambient, and tunable way for depositing localized metallic nanoparticles, FLaSk dewetting combined with LILPVD can be applied to applications in plasmonic metasurfaces, such as those employed in surface-enhanced Raman scattering (SERS), in-plane wave guides, and plasmonics for photovoltaics and other applications including as seeds for the growth of other nanomaterials and substrates for self-assembly monolayers (SAMs). To highlight one of these applications, we utilize the LILPVD gold particles as a seed for the growth of zinc oxide nanowires (NWs), using a recently developed method for growing these materials from noble metals. Zinc oxide NWs are valued as piezoelectric and photovoltaic materials.

RESULTS:

**Single-Line Scans.** As can be seen in Figure 1b,d and f, in contrast to the trench-ridge features observed in the FLaSk dewetting of polymer thin films, the single-line scan films on both glass and fused quartz substrates form a trench-ridge-dot structure—a trench-ridge structure with ridges composed of capillary-driven dewetted gold islands. Such features clearly demonstrate that capillary and thermocapillary dewetting are occurring simultaneously—material has been moved from the center of the laser path to generate an exposed trench and thickened ridge, but the ridges break up into isolated particles or fingering structures. From the center of the laser path to the intact film, we can see a transition of morphology: (i) bare substrate, (ii) particles, (iii) fingers, (iv) films with holes, and (v) intact film.
The laser writing parameters, including writing speed, laser power, numerical aperture (NA) of the lens, and the substrate conditions, combine together to control the final geometry. Early experiments indicated that writing speed did not have a significant effect on results due to the dewetting process occurring at a faster rate than beam motion (Figure S1). As such, experiments were conducted at a fixed speed of 1000 µm/s. When the power increases, as seen in Figure 1c, e, and g, the trench broadens, and small particles begin to appear in the center of the trench. At the same time, larger particles form on the edge of the trench and hole formation in the continuous film becomes more obvious. The NA determines the laser spot size through the relation:\(^{52} D_0 = \left(\frac{4A}{\pi NA} \right)\). At NA 0.85, a continuous trench can be generated starting at 160 mW (Figure 1d) on the fused quartz substrate, whereas at NA 0.1, no continuous feature can be generated until the power is raised to 320 mW using a power step of 80 mW. At higher powers, the features generated by different NAs are also different. Rather than forming dispersed small particles in the trench, a low-NA scan (Figure 1f,g) leaves a greater number of larger particles in the center and forms less covered trench area than a high-NA scan (Figure 1d,e).

While borosilicate glass has a similar thermal conductivity to fused quartz, the single-line scan results are distinct. Figure 1h summarizes the trench width as a function of power for NA 0.85 for the two substrates, where the error bars show the standard deviation of the distance between the left and the right edges. While using the same laser writing parameters (Figure 1b and Figure 1d), at low power, the single-line feature on the glass substrate has a more-ordered edge than the fused quartz. At the same time, the trench is also wider on the glass substrate at low power. When the laser power is increased, however, the width of the trench region on the fused quartz is larger than
the glass substrate (Figure 1h). Finally, while large particles tend to dwell at the tips of the fingers on the fused quartz substrates, the majority of large particles tend to pinch off on the glass substrate.

**Figure 1.** (a) Schematic of difference between conventional dewetting (top) where heat leads to coarsening of regions of the film to minimize overall surface energy and thermocapillary dewetting (bottom) where flow down thermal gradients transports material to cooler regions of the sample. (b-g) Scanning electron microscope (SEM) images of single line scans. (b) NA 0.85 160 mW single line FLaSk treatment on gold on glass. (c) 720 mW single line FLaSk treatment on glass substrate. (d) NA 0.85 160 mW single line FLaSk treatment on gold on fused quartz. (e) NA 0.85 720 mW single line laser dewetting on gold on fused quartz. (f) NA 0.1 320 mW single line FLaSk
treatment on gold on fused quartz. (g) NA 0.1 720 mW single line FLaSk treatment on gold on fused quartz. The white contrast is caused by the charging of exposed insulating substrates and the asymmetry of the pattern in (a) and (b) arises from slight distortion in beam shape due to manual calibration. Scale bar is 5 μm. (h) Measured width of the FLaSk single line dewetted gold film on fused quartz and borosilicate glass substrates at NA 0.85. The error bar is the standard deviation of the width in a single trench.

**Multi-Line Scan Results: Morphological Influence of Scanning Distance.** Multi-line laser scans were conducted on gold films on different substrates to investigate the overlap effect of FLaSk dewetting of gold. Figure 2a shows optical images of overlapping line scans at 720 mW, 1000 μm/s, NA 0.85 on a borosilicate glass substrate at a scanning distance of 0.19 μm for an increasing number of lines. The single line width for these conditions is 9.27 μm ± 1.22 μm. Strong signs of LSPR emerge at this scanning distance after around 80 scans. In scanning electron microscope (SEM) images (Figure S3), when the scanning distance is 0.19 μm, charging due to exposed glass is limited to only the edge of the pattern, which is consistent with the transparent line observed in the optical image.

Figure 2b shows particles formed at a few select laser parameters to highlight characteristic effects. For a lower NA (0.25) at a close spacing (0.19 μm), morphology evolves from large particles with considerable visible substrate damage at 160 mW to a few larger particles at 240 mW, to all small particles at 720 mW. Holding the same power, switching to a higher NA (0.85), and changing the line spacing reveals that there is a transition from smaller particles at 0.19 μm, to a bimodal mix of particle sizes at 2.48 μm, to separated lines at 4.19 μm.
Figure 2. (a) Morphology of overlapping line scans for 15, 20, 25, 30, 35, 40, 80, 160, 240, 320, and 640 scans. Scale bar is 50 µm. (b) SEM images of the center regions of the overlapping line scans, where (i – iii) show morphologies obtained using a NA 0.25 lens with a scanning distance of 0.19 µm at powers of (i) 160 mW, (ii) 240 mW, and (iii) 720 mW and (iv - vi) show morphologies obtained using an NA 0.85 lens at 720 mW with scanning distances of (iv) 0.19 µm, (v) 2.48 µm, and (vi) 4.19 µm. Scale bar is 1 µm in the main image and 100 nm in the inset.

To further investigate the relationship between overlap effects and the generated particle size, the same experiments were repeated with different NA objective lenses. Figure 3a shows optical
images of several characteristic scanning distances with NA 0.85, 0.25, and 0.1, with Figure 3b and 3c showing the results for particle size, density, and distribution in the overlapping regime. In Figure 3a, from left to right, the different columns show the optical images using NA 0.85, 0.25, and 0.1, where from top to bottom different rows contain the films made using 0.19 µm and 3.05 µm scanning distance. All images show plasmonic color indicating locally uniform densely packed nanoparticles. At a small scanning distance, the generated films are optically uniform but while decreasing the NA, the uniformity is increasing until some sign of instability shows up at NA 0.1 (Figure 3a iii). Increasing the scanning distance gives the uniform-nonuniform transition as illustrated before. However, although rather nonuniform features appear both at high NA (Figure 3a iv) and low NA (Figure 3a vi), their appearances are distinct: from a high NA to a low NA, the morphology is changing from strings of large particles mixed with patches of nanoparticle clusters (Figure 3a iv) to strings consisting of different sizes of particles (Figure 3a v and Figure S5 p) and at last, relatively uniform distributed big particles surrounded by light color smaller particles (Figure 3a vi). The particle size distribution does not change much with scanning distance, but the change is more significant with NA. With NA decreasing, the average particle size is larger and the particle size distribution is wider, which is also in consistent with what is observed in the optical images (Figure 3a). More details of the multi-line scan can be found in the Supporting Information.
Figure 3. Particle size distribution with scanning distance on borosilicate glass. (a) Optical pictures of multi-line scans using different NA and line spacing: (i) 0.19 μm NA 0.85, (ii) 0.19 μm NA 0.25, (iii) 0.19 μm NA 0.1, (iv) 3.05 μm NA 0.85, (v) 3.05 μm NA 0.25, and (vi) 3.05 μm NA 0.1. Scale bar is 20 μm. (b) Average particle size and particle density of the particles generated by multi-line laser scan. The error bars are standard deviations. The NA 0.1 curve is plotted in dashed line since the larger particles are so widely distributed such that they might not appear in the image. (c) Cumulative distribution of the nanoparticles of 0.19 μm using different NA. All particles smaller than 10 nm are considered noise in the image processing process.

Multi-Line Scan Results: Morphological Influence of the Substrate. Multi-line FLaSk scans were conducted on both borosilicate and fused quartz substrates using a laser power of 720 mW and NA 0.85 with scanning distance between 0.19 μm and 4.95 μm (Figure 4a). While a multi-
line scan on a glass substrate results in an optically uniform pattern with plasmonic color until a scanning distance of 3.05 µm, a fused quartz substrate can only maintain the uniformity at the smallest scanning distance used in the test (0.19 µm). At the right edge of the trenches, which is the position to the right of the last laser scan, the accumulated gold particles are larger on the fused quartz substrate.

![Figure 4](image)

**Figure 4.** (a) Images of NA 0.85 720 mW 1000 µm/s multi-line laser scans on fused quartz (top row, i-iv) and glass substrate (bottom row, v-viii). The scanning distances used are: (i,v) 0.19 µm, (ii,vi) 3.05 µm, (iii,vii) 4.00 µm, and (iv,viii) 4.19 µm. The length of the scale bar is 20 µm. (b) Schematic drawing of LILPVD. From top to bottom, the layers are: acceptor, gold thin film, borosilicate glass slide.

**Laser Induced Localized Physical Vapor Deposition Transfer Print Test.** During the multi-line laser scan tests, a morphology of small gold particles laying on top of bulk films was found on both sides of the laser-exposed region. At a laser power of 720 mW, NA 0.85, and a scanning distance of 0.19 µm, this phenomenon was found both on the glass substrate and the fused quartz substrate when the number of scans exceeds a certain threshold. It can even be found on the glass
substrate in the single-line features (Figure S10c). This is neither a thermocapillary or capillary dewetting effect nor a combination of thereof, but rather PVD.

The presence of PVD is confirmed by putting a silicon wafer superstrate “acceptor” on top of the gold on borosilicate glass “donor” sample and applying multi-line writing on the donor (Figure 4b). The acceptor then can catch the plume generated by the melted gold, and the particles are deposited onto the acceptor layer. By using different powers, particles with different size and distribution were coated on the acceptor (Figure 5c-f). While increasing the power from 320 mW to 720 mW, the larger particles inside the pattern disappear on the donor but the average size of the particles on the donor is not changing significantly. The changes in the particle size on the acceptor with power are also small in the tested range but when the power increases to 480 mW, a portion of the particles concatenate together, changing the measured particle size. The width of the LILPVD generated pattern on the donor and the acceptor are all increasing with power, where the width change of the donor shows a similar trend with the behavior of a single-line dewetting feature with increasing laser power.
Figure 5. (a) Simulated thermal profile by fixing the peak temperature at 1064°C (b) Schematic drawing of the profiles of dewetting on solid (upper) and dewetting on liquid (lower) (c) LILPVD particle size and density changing with laser power using NA 0.25 scanning distance 0.19 μm (d) LILPVD acceptor particle size vs acceptor particle size (e) LILPVD acceptor particle density vs donor particle density (f) LILPVD acceptor pattern width vs donor pattern width. The color shows the power used for the laser writing.

ZnO Growth Using Laser Induced Localized Physical Vapor Deposition Transfer Printed Gold Nanoparticle Seeding Layer. Using the LILPVD transfer printed gold particles as seeding
layer, zinc oxide NW arrays are grown (Figure 6 a, b). To achieve a high-density zinc oxide NW array growth, a higher power is needed for a larger scanning distance. Though the diameters of the NW seem not to depend heavily on the scanning distance nor the power of the laser writing at this condition (Figure 6 c). However, the density of the NWs shows a positive correlation with the laser writing power. Additionally, the NW array shows a narrower waist width than the corresponding gold nanoparticle pattern printed to the acceptor (Figure 6 d), and the NW density is positively correlated to the NW array width (Figure 6 e).

**Figure 6.** Hydrothermal growth of zinc oxide NW arrays using LILPVD transfer printed gold nanoparticles seeding layer. (a) SEM image of the hydrothermal zinc oxide NWs grown on LILPVD transfer printed gold nanoparticle seeding layer for different powers and scanning
distance for NA 0.25. (b) SEM image of the zinc oxide array grown on the LILPVD transfer printed seeding layer using a parameter setting as NA 0.25, 720 mW, 0.19 μm scanning distance. (c) Plot of diameter and density of the zinc oxide NWs measured manually from SEM images. (d) Plot of apparent waist width of the LILPVD transfer printed gold nanoparticles patterns and the grown zinc oxide NW arrays. (e) Widths from (d) plotted against zinc oxide NW density with the linear fit of the NW waist shown as guide for the eye where the unfilled red points indicate the width of the gold nanoparticle pattern.

DISCUSSION

**Single-Line FLaSk Dewetting: Evolution of a Single Line.** Due to the high mobility and surface energy of metallic melts, gold film thermocapillary patterns rapidly arrive at their terminal morphology. An order of magnitude prediction from dimensional analysis is possible, which indicates an upper bound for the thermocapillary dewetting time of ~1 ms for NA 0.1 and ~10 μs for NA 0.85 (see Supporting Information), which is <10% of the exposure time. Consequently, for a given experiment, the morphology of the line depends only on the values of laser power, scanning distance, and NA. Beyond this, it is difficult to predict the maximum temperature achieved during a FLaSk experiment, as the rate of evolution is commensurate to the time to thermal equilibrium and the gold film is the source of the heat. The evolution of the feature will continue until the removal of the heat source from the laser spot by dewetting arrests the dewetting process. Indeed, all that can be known with certainty at this time is that the melting point of gold (1064 °C) is reached at the beginning of the evolution of the film. A finite element method (FEM) model of the temperature profile at the point that this temperature is reached is shown in Figure 5a, along with
the relative gradient magnitudes, for different NA exposures (details in Supporting Information). This state serves as a context for future discussion, even if it only exists transiently on the way to a more dynamic system. Further, it may be taken as known that the melting point is reached in a region commensurate to the line width during some point of the morphological evolution. It is important to note that this point does not have to be at the start of the exposure. Much as with the ARC effects discussed above in dewetting polymer films,\textsuperscript{23-24} gold will absorb to a greater or lesser extent at different thicknesses. As a result, thicker regions that form during the dewetting may reach a higher temperature than the initial film (the opaque thickness of gold is ~60 nm). One implication of this is powers that are barely sufficient to create single-line patterns will still be able to completely dewet material in the ridge during multi-line patterns.

In contrast to the features formed when polymeric samples are subjected to FLaSk excitation, the metallic film’s island-hole formation is more typical of conventional large-area dewetting. Upon laser irradiation, the gold film heats to a temperature above the melting point and is moved down the thermal gradient by the thermocapillary force. The melt moved from the center of the laser spot then accumulates at the edge of the previously-generated melt pool. Simultaneously, there exists a competition between the thermocapillary force and the capillary force. For the high laser powers we most-often employ, this competition plays out at a rate much faster than the writing as discussed above and shown in Figure S2, but it can be observed in single-point writing at the lower end of laser powers, as shown in Figure S1 for 140 mW. By exposing for the lowest times our shutter allows, we can get a sense of the evolution with time. At the region of maximal thermal gradient, which is slightly off-center, the thermocapillary force dominates and results in dewetting of the film at early times in a trench-ridge morphology. As the heat is sustained,
however, the reduction in radial gradient away from the center of the beam allows for droplet formation, finger instability, and further from the heat source, hole formation, which is most-likely the result of solid-state dewetting\textsuperscript{53-55}. Therefore, the competition between the two forces will lead to different morphologies and will vary based on the patterning parameters. Moving to the line results, while using a higher NA lens the laser spot size is more confined, thus giving a larger thermal gradient. As a result, the thermocapillary force generated is higher, which means that at the center of the trench, more molten gold can be pushed away from the laser spot using the same laser power (Figure 1e). In contrast, the thermocapillary shear generated using a low NA fails to compete with the capillary force even at the center of the trench, so large particles remain there (Figure 1g).

The discussion to this point is equally valid for single spots and for lines. Once the beam begins to move from the initial spot, it will progressively interact with the ridge formed in the initial dewetting. Once the laser spot hits the edge of the built-up ridges, the newly-heated material will repeat the dewetting process, except at a larger material thickness and thus higher temperature. One implication of this is that the material that dewets beyond the initial formation may never again receive the full central laser power, as it will dewet from the approaching beam. Further, since the laser spot is only heating the material in front of it, the resultant profile will no longer be Gaussian, and, as with the ARC case, it will favor motion of material from the front of the laser to the sides.\textsuperscript{23} The net result is a steady state formation of side and front ridge that does not appear to lead to build-up of material. In the low NA case, it is possible that the gradient may be insufficient to push material on advancing of the laser spot. As discussed above, this will result in particles that remain in the center of the laser path thus receiving a larger dose of laser exposure and thereby
achieving temperatures sufficient to boil the gold. The SEM image (Figure 1e) of a single-line feature supports this conclusion, as can be seen by the localized regions of gold PVD surrounding the individual particles in the center of the line.

**Single-Line FLaSk Dewetting: Substrate Effects on Single-Line FLaSk Dewetting.** If we consider the quantitative results shown in Figure 1h, it appears as if the steady-state line writing width is linear with power. This observation is surprising as there are no linear behaviors in any of the governing equations of FLaSk dewetting. Setting this aside, it is interesting to examine the properties of the lines in the first quadrant to determine what conclusions may be drawn. For fused quartz, there is an $x$-intercept at 43 mW, which suggests that below this power the gold is no longer mobile. Above this power is a region at which, while some hole formation is observed, the thermocapillary force is not sufficient to dewet into a continuous trench until 160 mW. Above this point, the slope of the line arises from the balance of capillary and thermocapillary forces at increasing temperature and gradient. Interestingly, borosilicate glass, while also evincing linear behavior, has a $y$-intercept of 2.49 μm. This suggests that a line that could be written without any laser power. Convenient as this might be, clearly it is aphysical, and suggests a different mechanism is at play.

The major difference between the two substrates comes from the melting of the borosilicate glass during the process of FLaSk dewetting. The glass transition temperature of the substrate is 557 °C. It is therefore expected that the dewetting process should progress as a liquid-on-liquid dewetting, although the viscosity of the glass is difficult to predict. Silicate glass melts are non-Newtonian
and soften on increased shear rate, and the processing temperature of FLaSk is at least 500 K above the glass transition. This said, the melt viscosity of borosilicate glass near the melting point of gold is 4-6 orders of magnitude greater than molten gold in the absence of shear, so it is likely that the glass melt is more viscous than the gold. The net result would be deformation of the substrate during dewetting. The trench region of Figure 1b clearly shows the expected deformation as holes generated inside the trench.

If what we are observing in the borosilicate glass experiments is the result of dewetting of a low viscosity liquid on high viscosity liquid instead of dewetting on a solid substrate, the movement of the glass melt would be expected to reduce the motion of the gold melt by transfer of momentum at the interface. This explains the larger extent of dewetting on the quartz substrate at high powers. At low powers, the glass exhibits slightly wider trenches, which is most likely an effect of the increasing temperature of the ridge—when the dewetting is slower, these thickened regions may generate an instantaneously higher temperature and drive a greater region of overall dewetting. Were the dewetting to extend further down in power, it is likely that the glass viscosity would increase and the quartz and borosilicate results would collapse. Indeed, the lowest power point of the borosilicate results indicates a divergence from the linear trend in that direction.

**Multi-Line FLaSk Dewetting.** The spacing between lines in a multi-line writing process will have a large effect on how much material is heated. Restricting consideration to overlapping scans and keeping in mind that the single-line features have a size that is up to 9 times as wide as the expected laser spot size, there are four major mechanisms of material motion that can then occur. The first two are the usual ones that are observed in FLaSk (1) motion back towards the center of
the previous line and formation of microparticles and (2) motion in away from the center of the previous line to add to the ridge. The third is (3) PVD that occurs whenever the gold is molten. It is clear that (1) and (2) both result in (3), but an implication is that the same material can only be dewetted for a certain period of time at any given temperature without being completely redeposited through PVD. This redeposition takes the form of nanoparticles. PVD nanoparticles are not immediately apparent in single-line patterns due to insufficient time; however, repeated PVD will cause initially formed seeds to grow. Because of this range, multiple lines can add to the same population of nanoparticle. Adding to the complexity, nanoparticles will also dewet or redeposit should they encounter the laser beam in a subsequent pass. The fourth mechanism of motion is (4) capillary motion that occurs simultaneously with (1-3). For example, finger trenches on the edge of the first line feature, will either ball up then pinch-off into droplets due to capillary forces or be pushed away to the laser writing direction by the thermocapillary shear and pile up to form thickened film in subsequent scans. With increasing number of scans, the uneven distribution of material created by the capillary process will create greater texture in the thermal field and may cause the material to be forced towards regions of higher laser intensity. The net result is that the gold will remain in as a melt for even greater times, creating even more PVD redistribution in the region that is no longer subject to laser exposure. Any material that is instead pushed towards the ridge will result in thicker finger instabilities. The thicker fingers are going to repeat the pinching off-thickening cycle again and become droplets. All-in-all, this process is highly complicated, and it is important to consider what each parameter changes about the process.

**Multi-Line FLaSk Dewetting: Effect of Scanning Distance.** The scanning distance has an important role in terms of the formation of nanoparticles. While using a large scanning distance
can transport portions of the ridge inward to form microparticles and the PVD range will quickly be achieved, resulting in only a few lines contributing to nanoparticles. In contrast, with a small scanning distance, the laser is just writing inside the trench of the first line writing and therefore will interact with only a small portion of the ridge and any PVD deposited particles in the trench. In this scenario, many passes of the laser can add to the same generation of PVD particles. Because of this, larger scanning distances (Figure 2b and Figure S4-S8) will result in a mixture of microparticles and patches of small nanoparticles and smaller scanning distances will result in a greater number of larger, but more uniform particles. In intermediate scanning distances, stripes of larger and smaller nanoparticles without microparticles will be observed. The definitions of these regimes will depend most strongly on the NA.

**Multi-Line FLaSk Dewetting: Effect of Power.** As elaborated previously, power is a key factor during the FLaSk process in that it controls the peak temperature and the peak thermal gradient during the dewetting process. As seen in Figure 2b, the laser power is a dominant factor in controlling the morphology. At lower power, with power increasing, the morphology changes from bi-continuous holes (Figure S9) to large particles on exposed substrate (Figure 2b i). The morphology change indicates the dewetting type has changed from solid-state to liquid-state dewetting. Increasing the power even more increases the peak temperature and thus enhances the importance of the thermocapillary force and the PVD, enabling the establishment of the push-pull-PVD model. As the thermocapillary force is more dominant than the capillary force, instead of balling up locally to form submicron size particles (Figure 2b i), the molten gold is pushed and pulled before balling up. Along with the higher evaporation rate from the higher vapor pressure,
sub-100 nm densely packed particles are generated (Figure 2b iii) instead of sparsely distributed submicron particles.

**Multi-Line FLaSk Dewetting: Effect of Numerical Aperture.** The numerical aperture controls the size of the focused laser beam. While acting on absorptive material, different NA gives different peak temperature and thermal gradient, which would influence the competition of thermocapillary and capillary forces. Generally, a lower NA favors capillary forces and thus higher peak temperature during the laser writing process, since material is more likely to reach the highest power region of the laser. As a result, more microparticles are generated and left in the laser writing region like what we have seen in the single-line FLaSk dewetting. Larger redeposited particles are also expected due to the higher peak temperature. The larger spatial extent of the laser also leads to particle formation for larger scanning distances, though the particles formed in this case are smaller as only a few scans contribute to their formation. In consequence, the film written with a low NA results in a wider distribution of particles as shown in Figure 3b and c.

**Multi-Line FLaSk Dewetting: Effect of Substrate.** Though same test was done on both substrates (Figure 4a), the result of the multi-line FLaSk dewetting on glass substrates are more-desirable in that: (1) the densely packed particles morphologies could be generated with a much wider selection of scanning distances and (2) using same laser parameters, the patterns on glass are more uniform. It is clear that the melted substrate aids in the PVD process. The mechanism for this is the trapping of the molten gold, shown schematically in Figure 5b, which leads to (1) a higher gold melt temperature and (2) a longer dewetting time in each pass. Both of these effects lend to additional LILPVD by (1) higher vapor pressure and (2) a longer deposition time. This
explains why, for the same laser parameters, a relatively uniform nanoparticle film could only be generated at the lowest scanning distance on the fused quartz substrate (Figure 4a and Figure S8), while the degradation of the optical film uniformity is not seen until the scanning distance increases to 3.05 µm for the glass substrate (Figure 4a). This also explains why the building ridge on the right edge of the laser written region has larger particles on the fused quartz substrate than the glass substrate—more of the gold is being redeposited in the dewetting process on the glass and thus less is added to the ridge.

**Laser-Induced Localized Physical Vapor Deposition Transfer Printing.** As with any PVD process, it is possible to collect the plume on a proximate superstrate. The evaporation generated plume, if not collected by an “acceptor”, will eventually redeposit in the surrounding region. Due to the surface energy benefit, the plume deposits on the substrate in a Volmer-Weber mode and forms nanoparticles as the surface morphology. The material deposited is also subject to the laser heating from below. Although the intensity of the center point of the laser beam on the acceptor is no larger than ~3% of the intensity on the donor for the specific airgap thickness used, if applied repeated several times with overlapping, it could also contribute to the final deposited morphology through processes like dewetting or coarsening. Since the particles are generated through PVD, in comparison with other techniques of physical transfer, such as laser-induced forward transfer (LIFT), the resulting particles on the acceptor are of smaller size and more uniform morphology, though LIFT has been demonstrated for a wider range of materials. When compared with pulse laser deposition (PLD) and other conventional large-scale thermal PVD technique, LILPVD possess more versatility as a localized micropatterning method for due to its mask-free and ambient nature. With optimization of the parameters described above and
cautious control of the gap size, LILPVD can be further developed into a versatile technique for the printing of nanomaterials.

The plume size is expected to be larger than the laser spot since a large number of particles are deposited both to the left and right edge of the laser written region (Figure S10 a,b). The peak temperature, number of scans, and the size of the plume have some influence on the PVD generated particle size and distribution which can be tuned by the NA, scanning distance, power, speed and number of laser scans. The scanning distance and the NA, as discussed in the previous section, are the two key factors to control the uniformity of the final film and the size of the nanoparticles through the complicated mechanism described above. The power and speed, however, influence the particle formation in a more intuitive way: Increasing the power and decreasing the speed will generate a higher temperature in the irradiated region and elongate the laser treatment time. Higher powers and lower speeds result in more deposited material with larger particle size on the acceptor (Figure S10).

A comparison between particle sizes and densities on the donor and acceptor are shown in Figure 5c. The particle size on the donor substrate is not significantly altered with power from 320 mW to 720 mW aside from the large particles sparsely distributed in the lower power treated regions. Since the distance the laser spot moves after each scan is even smaller than the beam radius, although the power of the laser is increased, the melting front is still irradiated by the side region of the laser spot first. At 320 mW, the push-and-evaporate method has already been established though there are still large particles trapped inside the pattern because the thermocapillary shear is not able to push away the capillary force generated large particles as in the case of a low power single line dewetting process (Figure 1f). Increasing power, however generates less large particles
during the first laser scan, and the subsequent major movement of the melting front forms the rather uniform nanoparticle films on the donor. On the acceptor, the particle size begins at roughly the same as the donor but then shifts higher at higher powers. This indicates that, at these powers, the repeated exposure to the defocused beam is sufficient to coarsen the nanoparticles.

Figure 5f shows the comparative widths of the patterns as determined by detectable electron contrast in SEM. These results are relatively well fit by a linear correlation with slope 2.6 and an $x$-intercept of 13.2 μm. The $x$-intercept indicates the donor pattern width at which particles on the acceptor would become visible. This value is consistent with the point where coloration is visible on the donor. The slope corresponds to the spread in the plume on the way to the acceptor and is coupled to the loss in particle density of by a factor of ~2 shown in Figure 5c. The density reduction appears smaller than it should be considering that the plume broadening is in two dimensions, so such spreading should correspond to a reduction in density of more like 6.8. This source of this discrepancy is the limitation of the donor width to the patterned area—it can be expected that roughly an equal quantity of gold particles is being delivered to the surrounding gold film as to the area exposed by the laser. If we combine the density and width data, it would suggest that the actual width of the pattern on the donor should be ~1.8X greater than is visible, consistent with this explanation.

**Zinc Oxide Growth using Laser Induced Localized Physical Vapor Deposition Transfer Printed Gold Nanoparticle Seeding Layer.** The zinc oxide NW arrays grown from the LILPVD nanoparticles take the form of finite clusters of various orientation. This is consistent with the particles that they are growing from being large enough and unoriented enough to support multiple
NW facets. Consistent with the result shown in Figure 5c, the NW density of the grown zinc oxide structures increases with writing power without effecting the overall size of the wires (Figure 6c), also consistent with the seeds being super-critical, leading to no significant templating effect from the nanoparticle size. At low powers, the zinc oxide NW array is densest when grown on patterns made by smaller scanning distances, where at higher powers, the NW arrays tend to have a higher density at larger scanning distances. Since the nanowire density is correlated to the area covered by gold nanoparticles, this is an expected result of the transition from non-overlap to overlap. At low powers, increasing the scanning distance leads to regions of film that are skipped over, and thus to not contribute to the PVD. Once the laser spots are overlapping at higher powers, however, a larger scanning distance moves the laser beam closer to the previously built up ridge which results in a higher peak temperature during the PVD process, and thus a higher gold vapor pressure. The extension of PVD time and raised peak temperature combine together to tune the amount of gold printed onto the acceptor which in turn affects the NW array grown from the seeding layer. The fact that the apparent zinc oxide NW array width is smaller than the apparent width of the LILPVD transfer printed nanoparticle pattern (Figure 6d) and the positive correlation of the NW density with array width (Figure 6e) indicate that much of the SEM scattering in the gold patterns are coming from sparse nanoparticle arrangements, while the higher densities measured at the center of the patterns are in fact confined to a much smaller zone. This indicates that the size of the gold patterns is more related to the size of a single line plume, while the densest portions of the plume overlap in this narrower region.

CONCLUSIONS
Through single-line and multi-line FLaSk dewetting of gold thin films on fused quartz and borosilicate glass substrates with various combinations laser NA, power, and scanning distance different morphologies of gold microstructures and nanostructures are generated. This occurs through a combination of thermocapillary dewetting, capillary dewetting, and PVD. Capillary effects favor the formation of gold microdroplets, fingers, and perforated films, similar to conventional dewetting, while thermocapillary effects convolve these structures with the trench-ridge features synonymous with Marangoni dewetting. The balance of these two effects is determined by the NA of the laser, which defines the sharpness of the thermal gradient at a particular temperature and correlates with the thermocapillary mechanism. Due to the high vapor pressure of gold, the gold evaporates during the time that it takes for these features to form. Because of the increased time, the PVD effects are most apparent during multi-line patterns and are enhanced by overlap due to the finite range of the plume. By the proper selection of scanning distance and NA, all microstructures within the patterned gold thin films can be removed leaving only uniform gold nanoparticles. A lower NA has a larger scanning distance window for the nanoparticle generation, whereas a higher NA tends to generate more sharply distributed and densely packed nanoparticles. Perhaps most surprising is the effect of the selected substrate. Using borosilicate glass, a substrate with a glass transition temperature lower than the melting temperature of the gold, we broaden the patterning window for the nanoparticle films. This occurs due to the transition from liquid-on-solid to liquid-on-liquid flow, which slows the dewetting process and increases both the PVD time and temperature. The particle deposition method is verified by a LILPVD transfer print test where the vapor results in the formation of localized nanoparticles on a top superstrate. These transferred particles were used as the seeds for hydrothermal growth of zinc oxide NW arrays. In these transfer experiments, the particle size
appeared to be stable with respect to the laser parameters, revealing that the low temperature formation favors a specific size with variable density. This is a desirable feature for pattern repeatability, but a means to also alter the size, possibly by etching post treatment, would be beneficial for, for example, the seeding of single nanowires. Through these demonstrations, FLaSk has shown its ability of locally patterning or printing sub-100 nm nanoparticles with tunable particle density and size. The LILPVD transfer printing, as a vacuum-free PVD method for generating particles with different sizes, could be developed into a promising method for the scalable fabrication or rapid evaluation of optical metamaterials, sensors catalysts, and nanomaterials precursors.

METHODS

**Sample Preparation and Materials.** Borosilicate glass slides, fused quartz, silicon and FTO substrates are soaked in acetone for 20 minutes and then rinsed by isopropanol. The cleaned borosilicate glass and fused quartz slides are then transferred to an Anatech Hummer X sputtering system and sputtered gold films for 130s in argon atmosphere at 60~75 mTorr to achieve a thickness of 15 nm ± 5 nm as measured by a Bruker Dektak XT step profilometer. The gold films on borosilicate glass samples are used for the single line and multi-line FLaSk dewetting tests and the donor in the LILPVD tests. The fused quartz substrates are used only in writing tests and the FTO and silicon slides are only used in the LILPVD tests as acceptors.

**Laser Experiments: Apparatus.** Laser patterning is conducted on a custom laser apparatus. The samples are mounted on an MCL-MOTNZ integrated nanopositioning and micropositioning
stage with 95 nm resolution. The samples are placed facing the free-space FLaSk objective. An Opus 532 nm continuous wave diode-pumped solid-state laser provides the laser excitation. Power control is provided by an ISOMET IMAD-T110L-1.5 acousto-optic modulator (AOM), which is controlled by an NI-9263 data acquisition board with custom MATLAB software. Power is monitored by a Thorlabs power meter using a partially reflective mirror in the beam path. All patterning is conducted at manually-implemented focus.

**Laser Experiments: Single Line and Multi-Line FLaSk dewetting Tests.** The prepared gold films are secured to the laser stage with the gold layer facing the laser spike during the writing process. Laser scans are conducted on the gold films with parametric varying of scanning distance, power, and numerical aperture (NA) with a fixed writing speed of 1000 μm/s. Writing speed was not observed to have a significant effect on results (see Supporting Information). By translating the stage, the laser spike is moved on the gold thin film. Both single-line laser scans and multiple-line laser scans are conducted. Multiple-line scans are conducted in a region of 400 μm by 40 μm, the stage is moved 20 μm to the right and a single line scan is conducted using the same power and numerical aperture. For each test, we employ a fixed scanning distance, laser power, or NA.

**Laser Experiments: Laser Induced Localized Physical Vapor Deposition Transfer Print Test.** 200 mesh SiO₂ micro particles are mixed with corn syrup and water at a weight ratio of 1:10:10. The suspension is then applied to the four corners on top of the acceptor surface and is dehydrated at 85 °C for 15 min and then heated to 150~180 °C for 10 min. The donor film is then attached to the spacer suspension and squeezed to reduce the gap between the gold film on the donor and the acceptor. The airgap thickness is measured to be around 0.07 mm using a film
thickness gauge. The sample is cooled down to the room temperature in air and transferred to
thickness measurement by a thickness gauge. The sandwich structure was then annealed by the
FLaSk focused on the gold layer through the donor substrate. The annealing method used in the
LILPVD transfer print test is the same as the single line and multi-line FLaSk dewetting process.
The annealed samples are then soaked in DI water to remove the spacer layer.

**Zinc oxide Growth Using Laser Induced Localized Physical Vapor Deposition Transfer**
**Printed Gold Nanoparticle Seeding Layer.** Zinc oxide NWs are grown from the LILPVD seeds
following a previously-reported method.\(^6\) 0.77mL ammonium hydroxide solution (28.0-30.0% 
NH₃ basis in water from Sigma-Aldrich) and 0.114 g zinc nitrate hexahydrate (Sigma-Aldrich) are
mixed with 19.23 mL deionized water in a borosilicate glass vial to make an aqueous solution.
After vortex mixing the solution until it is clear, the silicon chip with LILPVD transfer printed
gold nanoparticles is placed inside the solution, angled face-down against the vial wall to avoid
excess precipitate buildup on the exposed side. The vial is then placed in an oven for 5 hours at 90
°C. After the growth, the sample is rinsed with ethanol and DI water before it is dried in air at room
temperature (25 °C).

**Measurement and Scanning Electron Microscope Imaging.** SEM images are taken using a
Zeiss Sigma Field Emission Scanning Electron Microscope at an acceleration rate at 3.00 KV or
5.00 KV. Line width tests are done using a self-designed code in MATLAB. SEM images taken
at a magnification no lower than 50 KX are used for the image processing for particle analysis.
Particle size distribution analysis is done using the particle analysis toolbox of the Fiji ImageJ
software. Local threshold methods are taken on the images to convert the SEM images into black and white images for the analysis.

ASSOCIATED CONTENT

Supporting Information.

This material is available free of charge via the Internet at http://pubs.acs.org.

Single dot exposure test, dimensional analysis of the dewetting process, SEM image of a multi-line laser dewetting region, details of multi-line laser dewetting with different scanning distance and numerical aperture, overlap multi-line laser writing with low power, evidence of LILPVD, LILPVD transfer printed to FTO, finite element thermal simulation (PDF)

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Notes

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