THERMOCAPILLARY AND ELECTROHYDRODYNAMIC MANIPULATION OF
SOFT MATERIAL IN THIN FILM AND LAMINATE DEVICE

By

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ABSTRACT OF THE DISSERTATION

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With thin film materials applied more ubiquitously to industrial applications, the demand for scalable low-cost thin film devices has surged. Generally, a tradeoff between device cost, efficiency, and speed has to be made during the manufacturing processes. As a result, challenges exist in exploring new mechanisms that enable the scalable fabrication and examination of thin film devices.

Among the non-cleanroom thin film manufacturing techniques, such as inkjet printing, gravure printing, and screen printing, most processes involve the manipulation of soft material in their liquid state. Due to the small scale of the material, capillary forces play an important role. The ability to control the capillary force using external fields is thus vital for these processes. With progress made on laser and electronic techniques, thermal and electrical methods to manipulate materials are on a higher technical readiness level. Specifically, this dissertation looks into applying extreme thermal and electrical field and the induced thermocapillary stress and electrocapillary stress to manipulate the flow of soft material in and out of plane for the synthesis, measurement of nanomaterials, and the design of scalable laminate device. Three aspects are investigated by this dissertation. (1) Focused laser spike (FLaSk) dewetting of gold thin film on glass
substrate: Parametric study of overlapping laser scans on gold nanofilm deposited on glass/fused quartz is conducted to unveil the influence of numerical aperture, laser power, and substrate effect. Through FLaSk dewetting of a gold thin film on a meltable substrate, densely packed nanoparticle arrays are manufactured in and out of the plane via laser induced localized physical vapor deposition. (2) FLaSk thermocapillary dewetting based thin film rheology for soft material films that uses an optical microscope to characterize the thin film’s flow behavior under thermocapillary stress: FLaSk Thermocapillary dewetted hole radius is used as a metrics for studying the soft material nano film’s rheological properties. By designing a multilayer heating substrate, a top material-independent thermal field is established and calibrated by melting of crystal material. Dot-exposure type FLaSk dewetting on nanofilms with different material composition and thickness is conducted. The nonlinear radii size evolution is captured by a stretched exponential function and the decay time is used for probing the film’s viscosity. Extracted viscosities on different films demonstrate how FLaSk thermocapillary dewetting can be used for probing rheological properties of thin films. (3) Switchable electrohydrodynamic(EHD) capillary bridge oscillator: The behavior of microliter sized opposing sessile droplets in ~ kV/mm electric field in a parallel plate capacitor is investigated. Based on whether the droplets could be actuated into a stable capillary bridge in electric field that is unstable without the electric field, the motions are characterized into multiple phases. The mechanism is explained by free energy analysis and experimental testing of fluids with various physical properties in different electric field and gap size. The study has enabled using electrocapillary phenomena to control the morphology change of microliter-sized droplets in a simple configuration suitable for the
design of a thin sheet device compatible with mass fabrication. Finite element method simulations are conducted in a combination of experimental results for the understanding of the physics. Progress made in each aspect of this dissertation could serve as the stepstone for the development of scalable ways of applying thermocapillary stress and electrocapillary effect for the rapid fabrication/characterization of low-cost thin-film devices.
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Figure 51. (a) Sawyer-Tower circuit for pyroelectric device characterization. (b) Schematic drawing of the EHD capillary bridge thermal switch with pyroelectric device (c) a top view of the 3 x 3 5µL castor oil droplets cast on a sapphire substrate coated with aluminum (d,e) The charge–field phase diagram and temperature on the back of the bottom sapphire substrate for system running without the EHD capillary bridge thermal switch as a blank comparison ran at 0.02 Hz, 0.5 duty cycle. The high voltage and low voltage for the PZT-5H are -500V and -400V. The top aluminum frame is heated to 80°C controlled by a custom PID controller built by LABVIEW. The temperature in (e) and (g) are the temperature monitored by an infrared thermal camera. The monitored area is the center ~ 1 cm × 1 cm of the back of the bottom sapphire. (f,g) The charge–field phase diagram (f) and temperature (g) on the back of the bottom sapphire substrate for system running with the EHD capillary bridge thermal switch

Figure 52. The max temperature on the back surface of a 1 mm thick ITO glass substrate while during the first bridging process of a 5 µL pure canola oil droplet vs. a 5 µL canola oil doped with 1.82% graphene 32.7% BaTiO₃ 0.34% Brij30. All concentrations are in weight percentage. 0 s is when the capillary bridge is established

Figure 53. (a) IR image of an EHD-CB thermal switch during on state: 3.5 kV, 1 mm gap size. The color bar shows the temperature. (b) The pixel value of a fixed point on the capillary bridge during the on state

Figure 54. (a-e) 7.5 uL of canola oil with 1 wt% 400 nm barium titanate nanoparticles subjected to manually applied 2.95 kV field to bridge and debridge a 4.62 mm gap. Grid size is 1 mm. (f) Side view during the first bridging (left) and after final debridging (right).
1. Introduction

1.1 Motivation and Scope of Work

During the past decades, progress has been made in the field of scalable production of thin film electronic device using roll-to-roll (R2R) printing in combination with printing techniques such as inkjet printing\(^1\text{-}^4\), spray coating\(^5\text{-}^7\), and slot die coating\(^8\). Combining the utilization of functional soft materials, the number of applications is surging in the field of organic light-emitting diodes (OLEDs)\(^9,^{10}\), organic photovoltaics (OPVs)\(^11\) and wearable sensors\(^12,^{13}\).

Due to the high surface-to-volume ratio, liquids at micro to nano scale are influenced dramatically by capillarity. Introducing other surface forces can enable additional control of the liquid flow, and therefore, there is a need to gain control over coupled surface forces for fluid manipulation.

Efforts have been undertaken in designing structures suitable for the printing of these devices and modification of their surface morphology to enhance the performance and lower the cost. Among these efforts, introducing external thermal field and electric fields are promising options as they are already used in processes like deposition\(^7\), sintering\(^14\), annealing\(^8,^{15}\). Recently, advances have been made on coating and patterning techniques using extreme thermal gradients and electric fields to achieve surface structures with high resolution in scalable methods. As a result, it is vital to have a better understanding of the role of extreme thermal/electric field induced transport phenomena and how to apply them in manufacture.

In the following sections of this dissertation, we will introduce: (1) Driving forces, governing equations, and important properties in FLaSk dewetting and switchable
EHD capillary bridge; (2) applying in-plane thermal gradient by FLaSk dewetting on metal thin film with a meltable substrate and making out-of-plane transfer printing of densely packed nanoparticle arrays as a synthesis method; (3) utilizing in-plane thermal gradient induced by FLaSk dewetting on polymer thin film for the probing of rheological properties; (4) using an extreme electric field for morphology control of a microdroplet as a controllable switch; (5) Outlook of possible improvements on FLaSk rheology and application of the EHD capillary bridge switch

1.2 Driving Forces and Governing Equations

This section generally reviews the capillary force, thermocapillary force, electrohydrodynamic forces, and their role in the systems included in this dissertation.

1.2.1 Surface Tension

Capillary tension is a contractional surface line force acting at any interface. Thermodynamically, one can also interpret it as excess energy coming from the limited interaction of surface molecules. When analyzed dynamically, it is typically converted to surface force by the introduction of Laplace pressure as the pressure difference between the inner fluid and the outer fluid:

\[ \Delta P = P_i - P_o = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  

(1)

, where the \( R_1 \) and \( R_2 \) denote the principal radii of the interface.

As a material property, the surface tension is subjected to changes from various factors, especially sensitive to the thermal field and chemical potentials. The change of
surface tension from changing of temperature or chemical potential is the well-known Marangoni effect.

1.2.2 Thermocapillary Forces

Thermocapillarity arises from the change of surface tension due to the change of temperature. It can be described by a surface shear origination from temperature gradient:

\[ \tau = \nabla \gamma = \beta \nabla T \]  

(2)

, with \( \beta \) being the Marangoni coefficient, in a typical range of \(-10^{-5} \sim -10^{-4} \, \text{N/mK}\). \(^1\text{6, 17}\)

The Marangoni number describes how strong the Marangoni effect is and is defined as:

\[ Ma = \frac{\beta L \Delta T}{\mu \alpha} \]  

(3)

, where \( \alpha = \frac{k}{\rho c_p} \) is the thermal diffusivity.

It is typically accepted that if \( Ma > 80 \), the Marangoni effect is playing an important role\(^1\text{7}\). Due to the progress made in microfluidics and laser-based technology, the application of thermal Marangoni forces in micro/nano manufacturing processes has increased during the last decades\(^1\text{6, 18}\).

The governing equation for capillary and thermocapillary thin film dewetting is the lubrication approximation of the Navier-Stokes equation:

\[ \frac{dh}{dt} = -\nabla \cdot \left( \frac{h^2 \beta \nabla T}{2\mu} + \frac{h^3}{3\mu} \nabla \left( \gamma \nabla^2 h + \frac{dV}{dh} \right) \right) \]  

(4)
, where \( \mu \) is the fluid viscosity, \( h \) the film thickness, and \( V \) encapsulates surface interactions, often negligible in thermocapillary dewetting.\(^{19}\) This equation has assumed a no-slip boundary condition\(^{19,20}\).

### 1.2.3 Electrohydrodynamic Forces

This section focuses on the EHD forces, governing equations, and dimensionless numbers for a liquid-air interface.

The electrostatic force is given by the divergence of Maxwell stress tensor:

\[
f_e = \nabla \cdot T_e = \nabla \cdot \left( \varepsilon \mathbf{E} \mathbf{E} - \frac{1}{2} \varepsilon \mathbf{E}^2 \mathbf{I} \right) = \frac{1}{2} \varepsilon \mathbf{E}^2 \nabla \varepsilon
\]  

, where \( \varepsilon \) is the permittivity \( \varepsilon = \varepsilon_r \varepsilon_0 \), where \( \varepsilon_r \) is the dielectric constant and \( \varepsilon_0 \) is the permittivity of vacuum \( \varepsilon_0 = 8.85418782 \times 10^{-12} \) \( m^{-3} \) \( kg \) \( s^{-4} \) \( A^{-2} \).

Based on the leaky-dielectric model\(^{21,22}\), the equations governing the behavior of the liquid-air interface for leaky-dielectric fluid in the air are listed below.

Continuity of incompressible fluid:

\[
\nabla \cdot \mathbf{v} = 0
\]  

Navier-Stokes equation for incompressible flow:

\[
\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = \text{Oh}(-\nabla p + \nabla^2 \mathbf{v}) \text{ in } \Omega_L
\]  

With \( \Omega_L \) being the liquid phase and \( \text{Oh} \) being the Ohnesorge number:

\[
\text{Oh} = \frac{\mu}{\sqrt{\rho \gamma R}}
\]  

The electric potential is given by:

\[ \nabla^2 \Phi = 0 \text{ in } \Omega_L \text{ and } \Omega_G \] (9)

The bulk density of free charge is 0 in the leaky-dielectric model\textsuperscript{21, 23} but the charge is allowed to transport inside the interface:

\[ \frac{\partial q}{\partial t} + \nabla_s \cdot (q \mathbf{v}) - \frac{1}{\rho_e} \nabla_s^2 q = \frac{1}{\alpha} \mathbf{n} \cdot \mathbf{E}_L \text{ on } S_f \] (10)

\( \mathbf{E}_L \) is the electric field on the liquid side of the interface \( S_f \) while \( \mathbf{n} \) is the unit vector normal to the interface \( S_f \). \( \nabla_s \) is the surface gradient. If we neglect the gravity, the electromechanical coupling on the interface can be obtained by applying the following equation:

\[ -Oh \mathbf{n} \cdot (-p + \nabla \mathbf{v} + (\nabla \mathbf{v})^T) = -2\kappa + 2Bo_\mathbf{E} \mathbf{n} \cdot || \mathbf{E} \mathbf{E} - \frac{1}{2} \epsilon \mathbf{E}^2 \mathbf{I} || \text{ on } S_f \] (11)

where \( \kappa \) is the interface's local mean curvature and the electric Bond number \( Bo_\mathbf{E} \) is defined as:

\[ Bo_\mathbf{E} = \frac{\epsilon_0 V^2}{\gamma R} \] (12)

and \( || \mathbf{A} || \) is the jump of a property \( \mathbf{A} \) across the interface.

The interfacial charge induces the jump of electric field across \( S_f \):

\[ q = \mathbf{n} \cdot (\epsilon_r \mathbf{E}_L - \mathbf{E}_G) = \mathbf{n} \cdot (\epsilon_r \nabla \Phi_L - \nabla \Phi_G) \] (13)

The Bond number \( Bo \) is defined as the ratio between gravity and surface stress:

\[ Bo = \frac{(\rho - \rho_g) g R^2}{\gamma} \approx \frac{\rho g R^2}{\gamma} \] (14)
Other characteristic values are also listed below.

Characteristic Properties:

Charge relaxation time, a characteristic time scale for the charge relaxation for the surface charge:

\[ t_e = \frac{\varepsilon_0}{K} \]  \hspace{1cm} (15)

Capillary time, from the balance between inertia and characteristic capillary pressure (Maxwell pressure \( \sim \gamma/R \)):

\[ t_\gamma = \sqrt{\frac{\rho R^3}{\gamma}} \]  \hspace{1cm} (16)

Viscous time, a time scale for viscous dissipation:

\[ t_\mu = \frac{\rho R^2}{\mu} \]  \hspace{1cm} (17)

Dimensionless charge relaxation time:

\[ \alpha = \frac{t_e}{t_c} \]  \hspace{1cm} (18)

Rayleigh limit, an upper limit for droplet charge before breaking into smaller droplets:

\[ q_R = \sqrt{\frac{64\pi^2 \varepsilon_0 \gamma}{R^3}} \]  \hspace{1cm} (19)

The R here is the radius of the charged droplet.
2. Focused Laser Spike (FLaSk) Dewetting of Gold Thin Films

Chapter 2 is reproduced with permission from Ma et al. 24, Copyright (2019) American Chemical Society.
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 force 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.
2.1 Introduction

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.\(^{25-31}\) 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, \(\beta = \frac{\delta \gamma}{\delta T}\) (where \(\gamma\) is the free-surface tension of the material). The Marangoni coefficient, in turn, determines the thermocapillary Marangoni shear, \(\tau = \beta \nabla T\).\(^{32}\) 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.\(^{16}\) 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.\(^{33-37}\) 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.\(^{33,34}\) 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,\textsuperscript{38} polymers,\textsuperscript{39-42} small molecules,\textsuperscript{43} liquid crystals,\textsuperscript{44} and metallic thin films.\textsuperscript{45}

Singer and colleagues’ work has heretofore investigated the application of FLaSk dewetting to polymer thin films\textsuperscript{46-48} and more recently, the consecutive dewetting of polymer-metal bilayers.\textsuperscript{49} 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;\textsuperscript{48} (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;\textsuperscript{46} (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,\textsuperscript{46} which have since been shown by Elashnikov \textit{et al.} to also arise in high-speed FLaSk dewetting;\textsuperscript{50} 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.\textsuperscript{47} 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.\textsuperscript{51} In addition, metals tend to have high surface tensions. This is readily apparent in Ferrer et al.’s examination of FLaSk heating of microdroplets and microfilms of metals, specifically bismuth and tin.\textsuperscript{45} In this work, it was observed that microdroplets, when heated with a $\sim 33 \mu m$ 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 et al. in early work on laser curing of gold inks.\textsuperscript{52} 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 3a and Figure 2). However, although considerable research has been conducted on laser and non-laser dewetting of metal thin films,\textsuperscript{53-57} 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.\textsuperscript{58} 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.\textsuperscript{59} This allowed for the rapid fabrication of zinc-based microcircuits.

This chapter 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.\textsuperscript{60-62} 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),\textsuperscript{63} \textsuperscript{64} in-plane waveguides,\textsuperscript{65} and plasmonics for photovoltaics\textsuperscript{66} and other applications including as seeds for the growth of other
nanomaterials\textsuperscript{67-70} and substrates for self-assembly monolayers (SAMs).\textsuperscript{71} 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.\textsuperscript{69} Zinc oxide NWs are valued as piezoelectric and photovoltaic materials.\textsuperscript{72-74}

2.2 Methods

2.2.1 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.

2.2.2 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.

![Diagram of FLaSk dewetting apparatus schematic drawing](image)

**Figure 1.** FLaSk dewetting apparatus schematic drawing.

2.2.3 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 section 2.2.1). 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.
2.2.4 Laser Experiments—Laser Induced Localized Physical Vapor Deposition Transfer Print Tests:

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.

2.2.5 Zinc Oxide Growth Using Laser Induced Localized Physical Vapor Deposition Transfer Printed Gold Nanoparticle Seed Layer:

Zinc oxide NWs are grown from the LILPVD seeds following a previously-reported method. 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).

2.2.6 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.

2.2.7 Finite Element Thermal Simulation

A finite element method(FEM) simulation of the thermal profile generated by a single laser spot is done using COMSOL Multiphysics. A Gaussian boundary heat source is fixed on the center of a 2D axisymmetric silica glass disk. Different peak powers are used for comparison of the different thermal profile generated from different NA at the same peak temperature (melting point of gold). A convection heat transfer boundary condition is applied to the heated surface while the other two surfaces are fixed at 300K. The detailed parameters are listed here:
Table 1. Parameters of the FEM thermal simulation

<table>
<thead>
<tr>
<th>Parameters and Variables</th>
<th>Equations or Value</th>
<th>Physical Meanings</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>5 mm</td>
<td>Radius of simulated cell</td>
</tr>
<tr>
<td>T</td>
<td>1 mm</td>
<td>Thickness of simulated cell</td>
</tr>
<tr>
<td>H</td>
<td>$5 \frac{W}{(m^2 \cdot K)}$</td>
<td>Heat transfer coefficient of air</td>
</tr>
<tr>
<td>NA</td>
<td>0.1,0.25,0.65,0.85</td>
<td>Numerical Aperture</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>532 nm</td>
<td>wavelength of the laser</td>
</tr>
<tr>
<td>$P_0$</td>
<td>12.16,4.863,1.87,1.429 mW</td>
<td>Peak power for different NA</td>
</tr>
<tr>
<td>$w_0$</td>
<td>$\frac{2\lambda}{\pi NA}$</td>
<td>Radius of a laser spot</td>
</tr>
<tr>
<td>$I_0$</td>
<td>$\frac{2P_0}{\pi w_0^2}$</td>
<td>Peak laser intensity</td>
</tr>
<tr>
<td>$I$</td>
<td>$I_0 e^{-2r^2/w_0^2}$</td>
<td>Boundary heating Source</td>
</tr>
</tbody>
</table>

2.3 Results

2.3.1 Single Dot Exposure Test at a Low Power:

To probe the initial state of the focused laser spike dewetting of gold thin film, a single laser pulse test is done at 140 mW at a time series on both borosilicate glass and fused quartz substrates with a Numerical Aperture (NA) 0.85 objective lens. On the start of the exposure (Figure 2 b and 2 f), the gold is melted and forms a morphology that resembles the trench-ridge feature observed in the thermocapillary dewetting of polymer. This feature does not persist long enough on fused quartz for us to observe it directly. With
extended exposure time, the feature evolved to develop the finger instability and more satellite holes are forming surrounding the major hole formed in the center. This kind of feature evolution shows the competition of the thermocapillary force and capillary force during the process. At the beginning stage, the gold in the center of the laser spot heats up quickly and is simultaneously exposed to a large thermocapillary shear force. Thus the thermocapillary-driven flow dominates the final geometry of the feature. At the later stage, since the gold at the center of the laser spot has already been pushed outward, the heat source becomes a ring like heat source and although the thickened melt front could absorb more energy from the beam, it does compensate the decay of temperature and gradient intensity away from the center. As a result, the capillary force surpasses the thermocapillary force to dominate the flow. With the aid of perturbations and inhomogeneities in the film and imperfect Gaussian heat source and substrate, the finger instability is generated. The satellite holes far from the primary central hole most-likely arise from solid state dewetting, whose kinetics in this case does not compare with the thermocapillary and capillary dewetting.
Figure 2. SEM image of the FLaSk dewetted feature of the gold thin film on top of (a)-(e) fused quartz and (f)-(j) borosilicate glass substrates under laser excitation parameters of NA 0.85 140 mW with different length of exposure time (FWHM): (a)-(e) and (f)-(j) ~430 µs, ~590 µs, ~1.48 ms, ~0.01 s and 0.1 s. (k) shows the equivalent diameter of the primary
central holes, which is the diameter of a circle with the same area as the exposed area of the substrate.

2.3.2 Single Dot Exposure Test at a High Power.

Single dot exposure tests are conducted on gold films supported by both borosilicate glass and fused quartz substrates. With a single laser irradiation at 720 mW 0.1 ms, both films form into hole with fingers morphology. The equivalent diameters of the primary central holes are 6.85 μm on fused quartz and 7.16 μm on borosilicate glass substrate. Substrate damage is easily seen on the glass substrate. Compared with the low power morphologies (Figure 2e and 2g), there are more particles left in the center of the exposed central hole and the finger instability is more developed.

![Figure 3. SEM image of single dot exposure with NA 0.85 720 mW 0.1 ms on a gold film on (a) fused quartz substrate (b) borosilicate glass](image)

2.3.3 Dimensional Analysis of the Dewetting Process:

A dimensional analysis is done on the Couette flow as a simplified model of the dewetting process.
\[
\beta \frac{dT}{dr} = \mu \frac{dV_r}{dz} \quad (20)
\]

\[
V_r = \int dV_r = \frac{dT}{dr} \cdot \frac{\beta}{\mu} \cdot \int dz = h \cdot \frac{\beta}{\mu} \cdot \frac{dT}{dr} \quad (21)
\]

\[
\Delta t = \frac{\Delta r}{V_r} = \frac{\Delta r}{h} \cdot \frac{\mu}{\beta} \cdot \left(\frac{dT}{dr}\right)^{-1} \quad (22)
\]

Or

\[
dt = \frac{dr}{V_r} = \frac{dr}{h} \cdot \frac{\mu}{\beta} \cdot \left(\frac{dT}{dr}\right)^{-1} = \frac{\mu}{\beta h} \frac{dr^2}{dT} \quad (23)
\]

Among the equation, \( h \) is the film thickness, \( \beta \) is the Marangoni coefficient of molten gold, \( \beta = \frac{\delta \gamma}{\delta T} \). \( \mu \) is the viscosity of the molten gold and \( dr \) is the radius of the dewetted spot on the substrate.

From COMSOL simulation of single-spot laser heating, the \( dt \) is calculated according to different NA. The parameters and results are listed here.
Table 2. Parameters and results of the dimensional analysis

<table>
<thead>
<tr>
<th>Parameters and results</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$dT$</td>
<td>~1000 K</td>
</tr>
<tr>
<td>$h$</td>
<td>~10 nm</td>
</tr>
<tr>
<td>$\mu$</td>
<td>~$1 \times 10^{-3}$ Pa⋅s</td>
</tr>
<tr>
<td>$B$</td>
<td>~$-1 \times 10^{-5}$ N/m$^2$</td>
</tr>
<tr>
<td>$dr(NA , 0.1 , &amp; , NA , 0.25)$</td>
<td>~10 μm</td>
</tr>
<tr>
<td>$dr(NA , 0.65 , &amp; , NA , 0.85)$</td>
<td>~1 μm</td>
</tr>
<tr>
<td>$dt(NA , 0.1 , &amp; , NA , 0.25)$</td>
<td>~1 ms</td>
</tr>
<tr>
<td>$dt(NA , 0.65 , &amp; , NA , 0.85)$</td>
<td>~10 μs</td>
</tr>
</tbody>
</table>

With a laser writing speed of 1000 μm/s, by the time the molten metal moves 1 μm, the laser spot could only move 0.1 μm for low NA (NA 0.1 and NA 0.25) laser writing and 0.01 μm, which are much smaller than the dewetted spot size, which justifies the assumption that the dewetting speed is much faster than the laser writing speed in the main text.

2.3.4 Single-Line Scans

As can be seen in Figure 4b,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.

**Figure 4.** (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.

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 on single dot exposure 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.

As such, experiments were conducted at a fixed speed of 1000 µm/s. When the power increases, as seen in Figure 4c, 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: \( D_0 = \left( \frac{4\lambda}{\pi NA} \right) \). At NA 0.85, a continuous trench can be generated starting at 160 mW (Figure 4d) 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 4f,g) leaves a greater number of larger particles in the center and forms less covered trench area than a high-NA scan (Figure 4d,e).

While borosilicate glass has a similar thermal conductivity to fused quartz, the single-line scan results are distinct. Figure 4h 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 4b and Figure 4d), 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 4h). 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.

2.3.5 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 6a 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 5), 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.

![SEM image of a multi-line (640 paths) laser writing with NA 0.85 720 mW 1000 μm/s scanning distance 0.19μm](image)

**Figure 5.** SEM image of a multi-line (640 paths) laser writing with NA 0.85 720 mW 1000 μm/s scanning distance 0.19μm

Figure 6b 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 6.** (a) Optical images of overlapping line scans for 15, 20, 25, 30, 35, 40, 80, 160, 240, 320, and 640 scans using a NA 0.85 lens with a scanning distance of 0.19 μm at 720mW on gold film on a borosilicate glass substrate. 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 7a shows optical images of several characteristic scanning distances with NA 0.85, 0.25, and 0.1, with Figure 7b and 7c showing the results for particle size, density, and distribution in the overlapping regime. In Figure 7a, 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 7a iii). Increasing the scanning distance gives the uniform-nonuniform transition as illustrated before. However, although rather nonuniform features appear both at high NA (Figure 7a iv) and low NA (Figure 7a 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 7a iv) to strings consisting of different sizes of particles (Figure 7a v and Figure 9 p) and at last, relatively uniform distributed big particles surrounded by light color smaller particles (Figure 7a 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 7a). More details of the multi-line scan can be found in the next section.
Figure 7. (a) Optical images 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.

2.3.6 Details of Multi-Line Laser Dewetting with Different Scanning Distance and Numerical Aperture.

The gold on borosilicate sample is treated with a parameter set of NA 0.85 720 mW and 1000 µm/s and is subjected to multi-line FLaSk dewetting with scanning distances from
0.19 μm to 4.19 μm with a step of 0.19 μm. The average width of the single lines is 3.11 μm ± 0.30 μm from five measurements under SEM. The first degradation happens at a scanning distance of 2.48 μm, where the plasmonic color of the FLaSk treated region first becomes discontinuous. With scanning distance increasing, an increasing number of large particles begin to appear inside the FLaSk dewetted regions. More obviously, to the right of the region that does not have plasmonic color, big particles on the right edge of the grating are frozen there. Another phenomenon worth discussing lie in the FLaSk dewetted with large scanning distance (Figure 8q to Figure 8v). The generated plasmonic patches have a crater shape with one side open, resembling what we have discussed in the single-line FLaSk dewetting of gold thin film.
Figure 8. Optical images of multi-Line scanned gold thin film on borosilicate glass using an NA 0.85 objective lens with power at 720 mW with different scanning distances: (a) 0.19 µm, (b) 0.38 µm, (c) 0.57 µm, (d) 0.76 µm, (e) 0.95 µm, (f) 1.14 µm, (g) 1.33 µm, (h) 1.52 µm, (i) 1.71 µm, (j) 1.90 µm, (k) 2.09 µm, (l) 2.28 µm, (m) 2.48 µm, (n) 2.67 µm, (o) 2.86 µm, (p) 3.05 µm, (q) 3.24 µm, (r) 3.43 µm, (s) 3.62 µm, (t) 3.81 µm, (u) 4.00 µm, and (v) 4.19 µm. The red rectangle in (t) indicates a crater structure.

The multi-line FLaSk dewetting test was done with different NA on the same sample. The optical pictures are attached below. As described in the main text, the FLaSk generated films have different particle size distribution with different NA and different degradation
ways. At low NA scans with a small NA, due to the huge overlapping and higher temperature during the scans, Marangoni-Bénard cells arise\textsuperscript{78} (Figure 11a).

\textbf{Figure 9.} Optical images of multi-line scanned gold on borosilicate glass using an NA 0.65 objective lens with power at 720 mW with scanning distances (a) 0.19 µm, (b) 0.38 µm, (c) 0.57 µm, (d) 0.76 µm, (e) 0.95 µm, (f) 1.14 µm, (g) 1.33 µm, (h) 1.52 µm, (i) 1.71 µm, (j) 1.90 µm, (k) 2.09 µm, (l) 2.28 µm, (m) 2.48 µm, (n) 2.67 µm, (o) 2.86 µm, (p) 3.05 µm, (q) 3.24 µm, (r) 3.43 µm, and (s) 3.62 µm.
Figure 10. Optical images of multi-line scanned gold on borosilicate glass using an NA 0.25 objective lens with power at 720mW with scanning distances (a) 0.19 µm, (b) 0.57 µm, (c) 0.95 µm, (d) 1.33 µm, (e) 1.71 µm, (f) 2.09 µm, (g) 2.48 µm, (h) 2.86 µm, (i) 3.24 µm, (j) 3.62 µm, (k) 4.00 µm, (l) 4.38 µm, (m) 4.76 µm, (n) 5.14 µm, (o) 5.52 µm, (p) 5.90 µm, (q) 6.28 µm, and (r) 6.66 µm.
Figure 11. Optical images of multi-line scanned gold on borosilicate glass using an NA 0.1 objective lens with power at 720mW with scanning distances (a) 0.19 μm, (b) 0.76 μm, (c) 1.52 μm, (d) 2.28 μm, (e) 3.05 μm, (f) 3.05 μm, (g) 3.81 μm, and (h) 4.57 μm.

**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 12a). 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 12. (a) Optical 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.

2.3.7 Details of Multi-Line Scan Results on Fused Quartz Substrate

The same experiment done on the gold on glass sample is conducted on the gold on fused quartz sample using NA 0.85 and 720 mW. Without aid by defect, optically uniform film could only barely be generated using the smallest scanning distance, which is 0.19 μm. The piled up large particles on the edge of the laser written regions on the fused quartz substrate are also more obvious than the film on borosilicate glass substrate. The previously found “crater” structure is again found in the patterns treated with larger scanning distances, indicating the particle generation is from the elongated laser treatment of particles of which the movement is damped.
Figure 13. Optical images of multi-line scanned gold on fused quartz using an NA0.85 objective lens with power at 720mW with different scanning distances: (a) 0.19 µm, (b) 0.38 µm, (c) 0.57 µm, (d) 0.76 µm, (e) 0.95 µm, (f) 1.14 µm, (g) 1.33 µm, (h) 1.52 µm, (i) 1.71 µm, (j) 1.90 µm, (k) 2.09 µm, (l) 2.28 µm, (m) 2.48 µm, (n) 2.67 µm, (o) 2.86 µm, (p) 3.05 µm, (q) 3.24 µm, (r) 3.43 µm, (s) 3.62 µm, (t) 3.81 µm, (u) 4.00 µm, (v) 4.19 µm, (w)
4.38 \(\mu m\), (x) 4.57 \(\mu m\), (y) 4.76 \(\mu m\), and (z) 4.95 \(\mu m\). The large area of plasmonic color shown in (i) might be generated due to a surface defect in the substrate.

2.3.8 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 \(\mu m\), 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 17 c). 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 12b). 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 14c-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 14. (a) Simulated thermal profile by fixing the peak temperature at 1064°C (b) Schematic 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.
2.3.9 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 15 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 15 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 15 d), and the NW density is positively correlated to the NW array width (Figure 15 e).
Figure 15. (a) SEM image of the hydrothermal zinc oxide NWs grown on LILPVD transfer printed gold nanoparticle seeding layer for different powers and scanning distances 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.
2.4 Discussion

2.4.1 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 \( \sim 1 \text{ ms} \) for NA 0.1 and \( \sim 10 \mu\text{s} \) for NA 0.85 (see section 2.2.3), 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 14a, along with the relative gradient magnitudes, for different NA exposures (section 2.2.3). 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{46,47} 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 3 but it can be observed in single-point writing at the lower end of laser powers, as shown in Figure 2 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 dewetting70-81. 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 4e). 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 4g).

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. 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 4e) 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.

If we consider the quantitative results shown in Figure 4h, 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 4b 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.

2.4.2 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.
2.4.3 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 6b and Figure 8 – 11) 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.

2.4.4 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 6b, the laser power is a dominant factor in controlling the morphology.

When the power is low for the multi-line overlap laser writing, e.g., at 80mW using an NA 0.25 the film develops into a bi-continuous film following the solid-state dewetting of Au thin film\textsuperscript{54}. Damage of the substrate can be seen at this laser power (the red rectangle in the inset of Figure 16).
Figure 16. Multi-line laser writing with NA 0.25 80 mW, 1000 μm/s, and scanning distance 0.19μm

At lower power, with power increasing, the morphology changes from bi-continuous holes (Figure 16) to large particles on exposed substrate (Figure 6b i). The morphology change indicates the dewetting type has changed from solid-state\textsuperscript{81} 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 6b 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 6b iii) instead of sparsely distributed submicron particles.

2.4.5 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 7b and c.

2.4.6 Multi-Line FLaSk Dewetting: Effect of Substrate.

Though same test was done on both substrates (Figure 12a), the result of the multi-line FLaSk dewetting on glass substrates are more-desirable in that: (1) the densely packed particle 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 14b, 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 12a and Figure 13), 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 12a). 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.

2.4.7 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.\textsuperscript{87,88} 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 17a,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 17).

2.4.8 Evidence of LILPVD

During the multi-line laser scans with overlap scanning distance, particles are deposited far away from the laser spot both on the left and right side of the laser written
regions (Figure 17 a and b). The growth of the nanoparticles is more clearly demonstrated with different number of laser paths.

**Figure 17.** Regions close to the edges of laser written area: (a) the left edge of a 40 μm laser written region with NA 0.85, 720 mW, 1000 μm/s, and scanning distance 0.95 μm on a glass substrate (b) a region close to the right edge of a 40 μm laser written region with NA 0.85, 720 mW, 1000 μm/s, and scanning distance 0.95μm on a glass substrate (c) the left edge of one laser path on gold on glass substrate (d) a region to the right of 15 laser paths
on gold on glass substrate (e) the left edge of one laser path on gold on fused quartz substrate (f) 15 laser paths on gold on fused quartz substrate with NA 0.85 720 mW 1000 μm/s scanning distance 0.19 μm writing.

**Figure 18.** LILPVD Transfer Printed to FTO. With different combinations of power and speed, particles with a different size and density are deposited through the LILPVD process onto the FTO acceptor using an NA 0.4 objective lens: (a)-(e) morphology of the acceptor with transfer printed nanoparticles. (f) Optical image of the corresponding donor regions, from left to right they are the donor regions for (b)-(e). The plasmonic color of the donor(Figure 18f) is showing the different size of particles on the donor. (g) The assembly drawing of the LILPVD transfer print test. From top to bottom, the layers are: glass slide (hollow blue rectangle), FTO glass (solid blue rectangle), 0.04 mm thick dehydrated spacer (green rectangles), gold thin film (yellow rectangle), borosilicate cover glass (blue hollow rectangle) and the laser beam from the objective lens.
A comparison between particle sizes and densities on the donor and acceptor are shown in Figure 14c. 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 4f). 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 14f 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 14c. 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.

2.4.9 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 14c, the NW density of the grown zinc oxide structures increases with writing power without effecting the overall size of the wires (Figure 15c), 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 does 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 14d) and the positive correlation of the NW density with array width (Figure 14e) 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.

2.5 Conclusion

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.
3. Focused Laser Spike (FLaSk) Thermocapillary Dewetting Based Thin Film Rheology for Soft Matter Thin Films

3.1 Introduction

The rheological properties are vital for the processing of soft matter thin films, from lab-scale preparation techniques like spin coating to industrial-scale techniques like blade coating, gravure coating etc. At the same time, supported nano thin films typically exhibit different properties from their bulk form from the molecular interaction with the substrate and the enhanced mobility of the free surface. As new functional soft material thin films emerging at increasing speed, it is thus natural to call on methods able to analyze the thin film deposited on substrate in situ at a high speed. Additionally, it is also of interest to investigate complex system’s thin film behavior such as nanoparticle composites, liquid crystals, and phase-separating blends. Similarly, additive manufacturing with high-performance bulk metallic glasses (BMGs) requires rapid extrusion before the BMGs crystallize and become immobile.\(^8\) That shear accelerates BMG crystallization, as demonstrated in past work,\(^9\) makes this process more challenging to execute. A thorough exploration of the processing parameter space for such materials will unlock new opportunities in the biomedical, aerospace, and microelectronics sectors.

To fill this gap in understanding, we propose to use thermocapillary (TC) shear as a materials-agnostic mechanical activation method to probe thin film materials. Previous research introduced focused laser spike (FLaSk) heating to generate thermal gradients up to \(\sim 1000 \text{ K/\text{	extmu}m}\) (Figure 14a), corresponding to \(\sim 10 \text{ MPa}\) of surface shear, for the dewetting of polymer and metallic thin films and the arrangement of block copolymers
In FLaSk, continuous wave laser excitation produces TC gradients with a high degree of spatial and temporal control. Through local softening, samples that are solid both before and after excitation lock in the effects of the exposure, such as dewetting or annealing. This is the key advantage of the approach—thermal gradients simultaneously provide both the mobility and driving force for assembly. Further, FLaSk allows for the evaluation of thin film properties in difficult-to-access (high temperature, high shear) conditions. Current methods for studying thin films cannot access this regime and require lengthy evaluations of materials on a whole-film level. As FLaSk experiments can occur over single-micron areas, a single microscope image can potentially measure thousands of experimental conditions on a single film. Further development will lead to \textit{in situ} optical analysis conducted live during chemical transformations or phase separation and growth.
3.2 Methods

3.2.1 Experimental

3.2.1 (a) Fabrication of Universal Heating Substrates

Figure 19. Schematic drawing of (a) heating substrates with an ARC (b) a UHS avoiding the ARC effect. (c) intensity profile of the red intensity of the optical image (e). (d) AFM measured height profile of the section line shown in (f). (c)-(f) are measured on a dewetted feature on a 150 nm thick PS 2 MDa film using 170 mW of 1s FLaSk annealing.

600 µm thick sapphire substrates (University Wafer 2561) were cleaned by acetone, isopropyl alcohol (IPA), and DI water. The substrates were then transferred to an electron beam evaporator and evaporated with 100 nm molybdenum and 10 nm aluminum in
sequence. The universal heating substrates were then kept in the air at ambient temperature for the oxidation of the aluminum layer. Without further inspections, $a < 4$ nm natural oxide layer was assumed to form on top of the aluminum.\textsuperscript{101, 102} Using a Thorlabs power meter, 92% of laser energy was measured to be absorbed by the heating substrate.

3.2.1 (b) Thin Film Preparation

<table>
<thead>
<tr>
<th>Material</th>
<th>MW (kDa)</th>
<th>$h_0$ (nm)</th>
<th>Bulk $T_g$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>4</td>
<td>150</td>
<td>~346</td>
</tr>
<tr>
<td>PS</td>
<td>35</td>
<td>50, 154, 200</td>
<td>~370</td>
</tr>
<tr>
<td>PS</td>
<td>280</td>
<td>150</td>
<td>~373\textsuperscript{103}</td>
</tr>
<tr>
<td>PS</td>
<td>2000</td>
<td>154</td>
<td>~374\textsuperscript{103}</td>
</tr>
<tr>
<td>TPD</td>
<td>0.517</td>
<td>150</td>
<td>~330</td>
</tr>
</tbody>
</table>

Table 3. Films tested in this work, the molecular weight, thickness, film preparation method, and the bulk glass transition temperature $T_g$ of the corresponding material.

For spin cast PS samples, the UHS was first cleaned with acetone, IPA and DI water. After the cleaning, 10 min of plasma cleaning at 100mTorr was carried by a plasma cleaner using air plasma. Dilute solutions of the polystyrene (PS) were made using propylene glycol methyl ether acetate (PGMEA). PS thin films with two MW were
spin cast onto the freshly-cleaned UHS. The same cleaning and spun coating procedures were repeated on Si wafers. Small molecule N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine(TPD) thin films in the stable glass (SG) state were made by physical vapor deposition (PVD) in a custom-built ultra-high vacuum chamber (base pressure $2 \times 10^{-7}$ Torr), at a substrate temperature of $(280 \pm 1)$ K (equivalent of 0.85 times the $T_g$ of bulk TPD), and deposition rate of $(0.20 \pm 0.02)\ nm/s^{104}$. The spin cast TPD film is made by spin coating following an annealing process at 75 °C for 15 min. The thicknesses of the PS thin films on the UHS were approximated by the measured thickness of the Si duplicates with a Filmetrics F-40 EXR spectroscopic reflectometer (which is more accurate on Si) while the TPD thickness was determined by spectroscopic ellipsometry (SE) using a J. A. Woollam M-2000V spectroscopic ellipsometer.

3.2.1 (c) FLaSk Annealing

The UHS was placed on the same three-axis 532 nm wavelength continuous wave(CW) Nd:YAG laser direct write system described in Section 2^{24}. The laser beam was focused onto the Mo layer of the UHS through a 1 mm thick borosilicate glass slide. Before tests on each film, the focus of the beam was manually adjusted by finding the sharpest brightest spot in the red channel of the camera from the photoluminescence signal. The tilt of the sample is compensated for in software from 3 alignment points by piezoelectric z-stage’s movement during translation.

Using a customized MATLAB program, FLaSk annealing was conducted on the UHS covered with different thickness of material using laser power ranging from 20 mW to 130 mW and exposure time from 0.1 ms to 10s. The center to center distance between
each test was at least 50 µm. Each power-exposure time combination was repeated at least 3 times on the same film.

3.2.1 (d) Feature Size Characterization

An AFM scan was conducted on one FLaSk dewetting induced feature (Figure 19f), an optical image was also taken on the same feature using a Leica DM2700 M microscope (Figure 19e). Comparing the profile of the AFM height map (Figure 19d) and the red channel of the RGB image (Figure 19c), we found the valleys in the red intensity correlate with the center point between the bulge peak and the valley bottom, which should be representative enough as the FWHM of the feature similar to what has been used in the previous work\textsuperscript{46}.

The peak location of the intensity map is then used to define the characteristic diameter of the dewetted features. Using a customized MATLAB code, we extracted the equivalent diameter of the dewetted features from the monochromatic intensity images.
3.2.1 (e) Image Processing

Figure 20. Optical microscope image of a FLaSk dewetting feature on a 150 nm TPD film using 130 mW 1s. The image on the left is the untreated RGB image. The image on the right is the feature’s red intensity, the asterisk shows the initial guess of the center of the feature while the yellow x shows the center after 5 iterations of the least square circle fitting process. The blue circle shows the circle found iteratively by the least square fitting of the eight sample points(red cross).

All the camera settings are kept the same while taking images for each film. Using a Leica MC70 HD optical microscope, a resolution of 67.16 nm/px is achieved.

The algorithm for the radius extraction is listed below:

1) Each image is cropped into 9 regions of interest (ROI) to include only the features from FLaSk dewetting. The steps following are all based on each ROI.

2) With the rings being the darkest feature in the ROI, each ROI is filled so the feature inside the dark ring is painted black.
3) The intensity of the grayscale image is integrated along the $x$ and $y$ axes, a Gaussian function fitting is applied to the integration to give an initial guess of the center of the ring feature.

4) 8 rays are cast out from the center found in step 3), with an angle of $45^\circ$ between nearest rays. The intensity versus the distance traveled along these rays are recorded.

5) The first peak of these intensity-distance plots is identified as a point on the ring we are trying to locate.

6) A least square regression method is applied to fit a circle through the 8 points found in the previous step.

7) The center of the ring is redefined using the ring found in step 6)

8) 5 iterations of 4) to 7) are repeated

3.2.2 Simulation

The simulation of the thermal profile was done using COMSOL Multiphysics. In an axisymmetric model, the laser beam was modeled as a Gaussian-shaped boundary heat source on the bottom surface of the Mo layer with a diameter given by equation $D_0 = \frac{4\lambda}{\pi NA}$, where $NA = 0.25$ is the numerical aperture of the objective lens, and $\lambda$ is the wavelength of the laser. The UHS was modeled as a three-layer structure of which the bottom is a 500 µm thick sapphire, the center layer is a 100 nm thick Mo layer, and the capping layer is 10 nm of sapphire. The simulation cell’s radius was set to 350 µm. A constant temperature boundary condition of $T = T_{amb} = 293.15 \, K$ was set to the bottom
of the substrate while a natural convection boundary condition was set to the side edges and the top surface of the substrate.

Figure 21. Max Temperature Over Time: Thermal history and hearing rate for the max temperature during FLaSk annealing. Solid lines are the max temperature and dashed lines are the heating rate at the center of the laser beam.

In the thermal simulation, the laser beam is modeled as a time dependent Gaussian shape boundary heating source. A rectangle function is used for setting the time-dependent heating. The laser power is assumed to ramp up to the full power or ramp down to 0 in 0.01 ms.

It can be seen > 98% of the heating processes finish in the first 0.2 ms, and then during the rest of the time, the film can be viewed to subject to a constant temperature boundary condition until the laser is turned off.

3.2.3 Power – Max Temperature Correlation

To calibrate the laser power – max temperature relation, laser exposure experiments with >1s exposure time and power up to 500 mW power were conducted on
the different crystalline materials (Figure 22-24). The samples were then examined by optical microscopy and/or AFM scans to find laser-induced melting at different powers to correlate their melting point with the first experimental sign of melting.

As the melting point suppression for metallic films is much weaker than their nanoparticle forms\textsuperscript{1-3}, by depositing a thin layer of crystalline material or using the layers existing on the UHS, we could find the sign of melting to get a sense of the max temperature during the process without influencing the heat conduction by a large extent. The color change in a test on TPD films also indicated that it could be the sign of melting of residual aluminum trapped between the capping oxide layer and molybdenum layer.

\textbf{Figure 22.} Optical microscope images where the circles are the evidence of melting of the residual aluminum. Images on the right are the zoomed-in view of the corresponding
features in the image on the left. As seen in the images on the right, the melting didn’t happen for the areas in green circles but can be seen in the red circle.

![Image of laser-induced damage](image)

**Figure 23.** Optical microscope image of laser-induced damage induced by laser exposures from 200 mW to 500 mW at 10s: the colored rectangles are showing where the lowest power to induce one new type of damage: green rectangles show where the substrate first get darker; orange rectangles show where the substrate starts to develop darker hole; the yellow sign shows where the substrate first produce black dots in the darker hole. Numbers on the bottom of the image shows the power used for the test in mW.

Another test was carried on a bare UHS using 10 s exposure time and power up to 500 mW at a step of 10 mW. As the aluminum layer deposited is smaller than 5 nm for this substrate, the sign of melting aluminum was not found. The first distinguishable change happened around 200 mW ~ 210 mW (green rectangles in Figure 23), which could come from the aluminum oxide’s phase transition into $\alpha$ phase. This is the most speculative temperature – power correlation for all materials used in the process. At ~ 310 mW, darker regions start to develop at the center of the laser spots (orange rectangles in Figure 23). Further increasing the laser power to ~ 350 mW, black dots can be spotted in the darker regions, possibly originating from the melting of the Mo layer.

The zoomed-in images can be found in Figure 24 with the same color of marks.
**Figure 24.** Simulated max temperature versus laser power and the laser-induced damage on the substrate at different power. Images on the right are the optical images of the laser-induced damages.

The theoretical melting temperature or the transition temperature are listed here:

<table>
<thead>
<tr>
<th>Material</th>
<th>Bulk Melting/Phase Transitioning Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>933.47</td>
</tr>
<tr>
<td>Gold</td>
<td>1337.33</td>
</tr>
<tr>
<td>$\alpha$-Al$_2$O$_3$</td>
<td>1323.15–1473.15$^4$</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2345.15</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2896.15</td>
</tr>
</tbody>
</table>

**Table 4.** Theoretical melting temperatures or the transition temperature of bulk material
Other than when the UHS was damaged at the highest temperatures, the correlation between the simulation and the literature results is strong.

3.3 Results and Discussion

3.3.1 Power - Max Temperature Correlation

The FEM thermal simulation gives a linear relation between the laser power and the max temperature achieved:

\[
T_{\text{max}} = 6.655P + 294.269 \, K
\]  

(24)

where the \( T_{\text{max}} \) is the max temperature in K and \( P \) is the power in mW.

The max thermal gradient in magnitude also has a linear relation with the laser power:

\[
(\nabla T)_{\text{max}} = -2.7 \times 10^6 P - 4.016
\]  

(25)

with a unit of K/m, the negative sign here is due to the fact that the temperature is highest at the center and lowest in the peripheral region.

To calibrate the power-max temperature relation, we conducted the FLaSk dewetting of an aluminum thin film and gold thin film. At a power step of 10 mW, the first power to dewet the gold film is 150 mW. The simulation result gives a max temperature of 1292.5 K, slightly lower than the melting temperature of bulk gold (1337.3 K), giving a relative error of 3.4%. In other experiments (Figure 22-24), the first distinguishable power of the aluminum melting (933.5 K) was found at about 95 mW, which relates to a max temperature of 926.5 K from the correlation, giving a relative
error of 0.76%. Taking the fluctuation of the laser power during the experiments of ~5%, the model seems to be able to accurately predict the relation between the max temperature and laser power, which we can then use in our evaluation of polymer thin films.

**Figure 25.** Simulation-Based Power - Max Temperature Correlation. (a) Simulated thermal (solid line) and thermal gradient (dashed line) profiles for three powers. (b) Max temperature vs power for two different exposure time with the horizontal dashed lines showing the melting point of bulk gold and aluminum and the vertical dashed lines showing the span where the first sign of melting is spotted during experiments. (c) An AFM height map of the tested spot on a 16 nm gold film with 150 mW, 1 s irradiation. (d) The optical microscope image of the same spot.
3.3.2 Radius Evolution

3.3.2 (a) Molecular Weight

Figure 26 shows the dewetting as a function of exposure time for PS films with four different MW. At a constant laser power \( T_{\text{max}} \), the dewetted radii show a quick growth during initial timesteps. The radii then grow slower and asymptotes a radius for each power. It might be questionable to use the max temperature \( T_{\text{max}} \) as the temperature metric as during the thermocapillary dewetting, the dewetting front is subjected to decreasing temperature as it is moving away from the center. However, this might be the most direct way to reflect the characteristics of the FLaSk dewetting process: A time independent thermal profile is established based on the max temperature and the growth model of different materials can be compared by applying the same thermal profile. Additionally, the highest temperature does set the most mobile region of the polymer, which may persist to some extent as heat transfer lags behind the dewetting. Other temperature metrics that better incorporate the evolving temperature during the dewetting
will be left as future work.

**Figure 26.** Radii versus laser exposure time for 150 nm PS films with four different MW: data points are the averaged radius of three repeated tests with the error bar showing the standard deviation of the tests. The curves are the stretched exponential fitting model for the corresponding max temperature using the averaged $R_{\text{max}}$ and $\tau$. The insets are the $\alpha$ term used for the fitting and the averaged and standard deviation of $R^2$ for all the fittings. Different color denotes different max temperature used in the tests.

As seen in Figure 26, visible dewetted feature start to appear at lower $T_{\text{max}}$ for films with lower molecular weight. This is not surprising as a higher MW relates to a higher $T_g$ and higher melt viscosity as discovered several decades ago. In addition, it
is apparent that for films with lower MW, the radius evolution happens at a faster rate thus, the radius asymptotes the max radius at a shorter time compared with their higher MW peers.

To capture these growth features of the radii, we employed a stretched exponential fit or the Kohlrausch–Williams–Watts (KWW) function which is typically adopted for the description of relaxation processes in disordered systems\textsuperscript{111-113} like the glass transition process of polymer\textsuperscript{113, 114}:

\[
R = R_{\text{max}} \left( 1 - \exp \left( - \left( \frac{t}{\tau} \right)^\alpha \right) \right)
\]  

(26)

, where \(R\) is the dewetted radius found by the image processing, \(R_{\text{max}}\) is an asymptotic max radius of dewetting over infinite time, \(\tau\) is the characteristic decay time constant for the dewetted radius to evolve to \(~\)63.21\% of the final \(R_{\text{max}}\), and \(\alpha\) here is the stretching exponent, which is typically shown as \(\beta\) in general literature. As each laser testing condition is repeated three times, we get three \(R_{\text{max}}\) and \(\tau\) for each testing condition and the results shown in subsequent figures are the average value of them.

The stretching exponent \(\alpha\) is obtained by optimizing the \(R^2\) value of the fitting for each film. For the PS films with \(~\)150 nm thickness, the \(R^2\) value of the stretched exponential is all above 0.9 while using constant \(\alpha\) values for all the max temperature probed. Compared with the two lower MW films, the PS 280k and PS 2M films are less completed of growth of radii as their asymptotic behavior \(R_{\text{max}}\) are not as apparent during the experimental heating time (\(~\leq\) 100 s).
Figure 27. (a). Max radii versus the max temperature for PS 150nm films with MW at 4kDa, 35kDa, 280kDa, and 2MDa from Equation 26. Error bars showing the standard deviation of three repeated tests with (b). a zoomed-in view of the max radii. (c). The decay time of the PS 150 nm films with MW at 4kDa, 35kDa, 280kDa, and 2MDa. The dash lines are the least square error fitting of the experimental data points using the Arrhenius fitting equation (Equation 27). The first data points for the 4k, 35k, and 280k films are excluded due to the visible error (as seen in Figure 3 for the very first curve). The first three data points of the PS 2M film is abandoned for the same reason. (d) The activation energy for the four PS films from the Arrhenius model. The error bars are showing the 95% confidence intervals.
The max radius $R_{\text{max}}$ and the decay time $\tau$ are extracted and plotted against the max temperature (Figure 27 a-c).

If we ignore the first data points that typically have a limited number of data points, for MW 4k, 35k, and 280k films, the $R_{\text{max}}$ increases with $T_{\text{max}}$ while $\tau$ decreases with $T_{\text{max}}$ increasing. This can be explained by the higher temperature and higher thermal gradient from higher power laser heating. One increases mobility, while the other one provides a stronger driving force. At a lower $T_{\text{max}}$, the difference between different MWs of the two values is larger, and this difference shrinks when $T_{\text{max}}$ shifts to higher values. This can be attributed to the viscosity’s (modified) Arrhenius relation with temperature\textsuperscript{106,115}. It is further clear that the decay time for higher MW is longer.

To better quantify these differences, the $\tau$ versus $T_{\text{max}}$ was fitted using Arrhenius relation, excluding the first, unstable data points in Figure 27.c:

$$\ln \left( \frac{1}{\tau} \right) = - \frac{E_A}{RT_{\text{max}}} + C$$  \hspace{1cm} (27)

The fitting information for the decay time versus Tmax is shown here:
<table>
<thead>
<tr>
<th>Molecular Weight (MW, Da)</th>
<th>4k</th>
<th>35k</th>
<th>280k</th>
<th>2M</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C</strong></td>
<td>-14.09</td>
<td>-17.44</td>
<td>-5.431</td>
<td>-23.1</td>
</tr>
<tr>
<td></td>
<td>(-15.43, -12.74)</td>
<td>(-18.77, -16.11)</td>
<td>(-19.73, 8.866)</td>
<td>(-68.68, 22.49)</td>
</tr>
<tr>
<td><strong>E_a</strong></td>
<td>6.205e+04</td>
<td>1.038e+05</td>
<td>4.768e+04</td>
<td>3.160e+05</td>
</tr>
<tr>
<td></td>
<td>(5.21e+04, 7.2e+04)</td>
<td>(9.395e+04, 1.136e+05)</td>
<td>(-7.748e+04, 1.728e+05)</td>
<td>(-1.595e+05, 7.915e+05)</td>
</tr>
<tr>
<td><strong>R²</strong></td>
<td>0.9389</td>
<td>0.9755</td>
<td>0.1609</td>
<td>0.1487</td>
</tr>
<tr>
<td><strong>RMSE</strong></td>
<td>0.3769</td>
<td>0.3763</td>
<td>0.9279</td>
<td>8.303</td>
</tr>
</tbody>
</table>

**Table 5.** Fitting results for equation 27 on 150 nm PS films with different MW

From Table 6, we see that the fitting for the lower MW(4k and 35k) films is better and the fitting is of lower quality for the higher MW films. This again comes from the limited length of experimental time. For lower MW films, most stages of radii evolution are completed during the probed time, while this is not the case for the higher MW ones. As a result, if the experimental data doesn’t include the asymptotic stage, the model would be more a prediction than a characterization. Within confidence bounds, a higher MW relates to higher activation energy (Figure 27. d), making the decay time more sensitive to the temperature.

Using the equation below, we define an effective viscosity for thermocapillary dewetting:

$$\mu = \frac{\beta \nabla T}{1/\tau} = \tau \cdot \beta \nabla T$$  \hspace{1cm} (28)
, where $\beta$ here is the thermal Marangoni coefficient, for PS it takes a value of $-8.85E-5$ N/mK. The $\nabla T$ takes the max value calculated from Equation 25. Using this equation, we derived the effective viscosity of the PS 150 nm films with different MW (Figure 28). It can be seen again the higher MW film subjected a larger viscosity change within the same interval of max temperature.

The probed effective viscosity’s higher bound is around the material’s viscosity at its bulk $T_g$, this match indicates the method could be used to probe the viscosity of a material. The fact that the value is typically higher than the model is due to several facts: (1) The temperature and gradient used here are the maximum values during the test (2) The film is a supported film, so the dewetting process will see the influence from the substrate. It is important to note of the second point that this was previously shown to not be a significant effect.\textsuperscript{46}
**Figure 28.** Derived effective viscosity of PS 150 nm films with different MW. The dashed lines here are the bulk viscosity of two bulk PS with similar MW using WLF model\(^{10}\). The vertical reference lines are the \(T_g\) of the two films while the horizontal reference lines are showing the upper and lower bond of the effective viscosity of the PS 4k and PS 35k films.

3.3.2 (b) Film Thickness

**Figure 29.** Radii versus laser exposure time for 35 kDa PS films with three different thicknesses: data points are the averaged radius of three repeated tests, the error bar showing the standard deviation of the tests. The curves are the stretched exponential fitting model for the corresponding max temperature using the averaged \(R_{max}\) and \(\tau\). The insets are the \(\alpha\) term used for the fitting and the averaged and standard deviation of \(R^2\) for all the fittings. Different color denotes different max temperature used in the tests.

To probe the ability of FLaSk rheology on film thicknesses. Tests were conducted on PS 35 kDa films with 3 different thicknesses. Figure 29 and Figure 30a shows that at the same power/ Tmax, the dewetted radius is largest on the thickest film. However, the thinnest film shows the largest viscosity and shortest decay time while the intermediate thickness one shows the lowest viscosity and longest decay time. The suppression of the
\( T_g \) for thinner supported films have been reported multiple times\(^{116}\) while the existence of substrate for the supported film and the interactions between the film and the substrate typically increase the viscosity. As a result, the film’s effective viscosity measured by existing methods typically shows an overall effective viscosity of the film influenced by both effects simultaneously. It is thus natural to have an optimal thickness that have the lowest viscosity when the film is subject to both effects from the free surface and the substrate, which we also see here in Figure 30 b,c. The activation energy for the dewetting rate shows a negative correlation with the film thickness(Figure 30 d). As the film thickness becomes larger, the film surface experiences less effect from the substrate. Since FLaSk rheology depends on the surface shear, the activation energy of the growth rate of the radii could represent the surface mobility (Figure 30.d).

A phenomenon worth noticing is the double step growth of PS 35 kDa 200 nm film. A clear plateau can be witnessed at about 1E-0.5 s. This phenomenon has been seen in a previous test on measuring surface and bulk relaxation of rupture created by nanoparticle embedded into polystyrene thin films\(^ {117}\). This double step growth mode confirms the higher mobility of film with thicker thickness.
Figure 30. (a). Max radii versus the max temperature for PS 35k films with film thicknesses at 50 nm, 150 nm, and 200 nm from Equation 26. Error bars showing the standard deviation of three repeated tests with (b). Decay time of the PS 35 kDa films with thicknesses at 50 nm, 150 nm, 200 nm. The dash lines are the least square error fitting of the experimental datapoints using the Arrhenius fitting equation (Equation.27). The first datapoints for the 4k, 35k and 280k films are excluded due to the visible error (as seem in Figure 27 for the very first curve). The first three datapoints of the PS 2M film is abandoned for the same reason. (d) The activation energy for the PS 35kDa films with different thicknesses from the Arrhenius model. The error bars are showing the 95% confidence intervals.
3.3.2 (c) Glass Former Type

Glassy material, except the commonly seen polymers, could also have form of small organic molecules (molecular glass) and metallic glass by extreme preparation conditions like sputtering or evaporation. Molecular glass, due to the small size of the molecules, can exhibit a much more enhanced surface mobility compared with their bulk form\textsuperscript{118}. Although the free surface enhanced mobility is ubiquitous, it is more obvious for molecular glass than polymers. This is due to the fact that polymers, even short-chain ones, interact more with the bottom layer of the film compared with the molecular glass due to entanglement effects\textsuperscript{119}. As a result, it is not surprising to see the double stage radii growing mode for a molecular glass film which doesn’t show for PS films with similar thickness (Figure 31). The plateau time for the first step is around 0.01 s~ 0.1 s, which is much shorter than the PS 35kDa 200nm film(Figure 29c), showing the surface mobility of the TPD film is higher.

**Figure 31.** Radii versus laser exposure time for 150 nm PS films with four different MW: data points are the averaged radius of three repeated tests with the error bar showing the standard deviation of the tests. The curves are the stretched exponential fitting model for the corresponding max temperature using the averaged $R_{max}$ and $\tau$. The insets are the
\( \alpha \) term used for the fitting and the averaged and standard deviation of \( R^2 \) for all the fittings. Different color denotes different max temperature used in the tests.

**Figure 32.** (a). Max radii versus the max temperature for 150nm films of PS 4kDa, 35kDa, and TPD. Error bars showing the standard deviation of three repeated tests. (b). the decay time for the PS 4kDa, 35kDa, and TPD films. The dash lines are the least square error fitting of the experimental data points using the Arrhenius fitting equation (Equation 27). The first datapoints giving problematic fittings are manually removed. (c) The activation energy for the TPD, PS 4kDa, and PS 35 kDa films from the Arrhenius model. The error bars are showing the 95% confidence intervals. (d) The effective viscosity of the TPD, PS 4kDa, and PS 35kDa film. The horizontal reference lines are showing the upper and lower bounds of the effective viscosity. The vertical reference line
shows the bulk $T_g$ of TPD. The solid lines with symbols are derived from experimental data, while the dashed lines with hollow symbols are from the WLF model of the corresponding bulk material.

Based on previous experimental and simulation studies\textsuperscript{12,26}, we expect the viscosity of the bulk TPD to be orders of magnitude lower than both PS homopolymers used in this work (Figure 32 d), with these differences becoming larger as the temperature is decreased (4-12 orders of magnitude). If $\tau$ is dominated by the bulk rheology, we would therefore expect it to be much smaller in TPD. On the contrary, the TPD film shows a larger $\tau$ at all temperatures than both the PS films (Figure 32 c).

From Figure 32 c, it can be seen that the activation energy is highest for the stable glass TPD film, followed by the 35 kDa PS, and then the 4 kDa PS. It is still a puzzle of the source of this effect. It is possible that for the TPD and PS 4k, as oligomer and polymer below entanglement, the slip\textsuperscript{120-122} during the dewetting process is playing some role or that there is some order that is induced by the shear, creating more stable pre-crystalline regions. Either way, these results demonstrate a quantitative measure of the mobility under shear of confined thin films that can be extracted from FLaSk rheology that probes chain entanglement and glass stability or fragility. The growth of the radii at constant temperature will be analyzed as future work to probe more into this model.

3.4 Conclusion

Using dot-exposure FLaSk dewetting and optical microscopy, we have discovered a high throughput metrology method for glassy thin film. The FWHM radii of the
dewetted crater generated by thermocapillary dewetting are extracted from the intensity map of optical microscope images. The fitting of the dewetted radii versus time using a stretched exponential model renders a characteristic time scale (decay time $\tau$) showing strong relation with the rheological properties of the film. An effective viscosity for thermocapillary dewetting is derived by using the decay time. From the experimental results, we can identify the change of rheological properties from the effect of molecular weight, film thickness, and glass former type, proving this technique is a viable micro/nano rheological measurement method. Further fitting of the decay time versus the max temperature reveals more a correlation between the activation energy and the surface mobility. Future work will utilize this metric to compare materials with different processing parameters, such as molecular weight, thickness, or the presence of mesoscale order, such as crystallinity or additional phases.
4. Switchable Electrohydrodynamic Capillary Bridge

4.1 Introduction

Liquid jet, capillary bridge, and the instability of slender liquid threads have been a topic that is studied by the fluid mechanics community for centuries ever since Da Vinci’s work hypothesizing that the drop’s detachment from a tap is determined by the gravity overcoming the cohesive forces.\textsuperscript{123, 124} The stability of a liquid bridge at the presence of an electric field has also been studied for decades. Multiple researchers have conducted studies on the stability analysis of liquid bridges of perfect dielectric\textsuperscript{125-128} and perfectly conductive\textsuperscript{129, 130} fluid with\textsuperscript{131} and without\textsuperscript{127, 128} the presence of gravity. In most of these studies, however, the contact lines are typically pinned on both ends for the ease of analysis. Nonetheless, these analyses have indicated the presence of such a field could help stabilize the capillary bridge against perturbations.

Petkov et.al\textsuperscript{132, 133} have analyzed the capillary bridge’s stability without electric field with unpinned contact lines between parallel substrates. Their study clearly shows for liquid bridges with a closer to $90^\circ$ contact angle could achieve a larger aspect ratio, i.e., bridge height vs. radius.

Mugele et.al\textsuperscript{129} have done a detailed analysis of the capillary bridge in axial electric field using perfectly conducting liquid with unpinned contact lines. In their work, they have their liquid cast on the opposing surfaces of a parallel plate capacitor with the substrates coated with thin dielectric layers. They blended water, glycerol and sodium chloride to achieve a contact angle of about 90 degrees. They claimed that droplets on opposing substrates would attract each other in the electric field and form a bridge eventually when the voltage is high enough. The contact angle of the capillary bridge
state follows the Lippmann equation\(^{134}\) in electrowetting on dielectric (EWOD): 

\[
\cos \theta = \cos \theta_y + \frac{\varepsilon_0 \varepsilon_r U^2}{2 \gamma_{lv} h_r} \varphi, \quad \theta, \ \varepsilon_r, \ \gamma_{lv}, h_r
\]

\(\theta\), \(\theta_y\), \(\varepsilon_r\), \(\gamma_{lv}\), \(h_r\) are the contact angle in the electric field, contact angle without electric field (Young’s contact angle), the dielectric constant of the insulation layer between the liquid and the conductive substrate, liquid-air interfacial energy, and the thickness of the insulation layer respectively.

In contrast, the droplets take the Young's contact angle without any contribution from the electric field. While the voltage is smaller than the critical voltage, the phase diagram is composed of three areas: droplets at large separation, capillary bridges at small separation, and a coexistence area at intermediate gap size. Of which the intermediate state's morphology is history-determined, \textit{i.e.} if initially the liquid is in droplets state, they will stay as droplets after the electric field is turned on and vice versa. Above a critical voltage, oscillations replaced the coexistence area and represents an unstable behavior of periodic oscillation between droplets and capillary bridges at a constant electric field. The authors attributed the oscillation phenomena from the electrowetting during the bridge state: the contact angle stayed relatively a constant value during the bridge state, but the wetting diameters get larger, which drives the bridge unstable and break it back into droplets. The droplets then repeat the initial process, attracting each other and then form the capillary bridge. The frequency of the oscillation is determined by the kinetics of the charge relaxation process through the insulation layers. The breaking of the liquid bridge in the oscillation process is claimed to be an electrowetting process with an advancing contact line and a constant contact angle.

Mugele et.al\(^{129}\)'s work has clearly shown the ability to use simple configuration to achieve the actuation of morphology change without any motion of the substrates.
However, the presence of the oscillation is not desired for the purpose of control as it has limited the length of the “on” state for the capillary bridge. Thus it is of interest to have a method to achieve a motion-on-demand-only capillary bridge.

In this chapter, we demonstrate that by using different liquids, gap sizes, and voltages, droplets with volumes $<15 \, \mu\text{L}$ placed in a parallel plate capacitor, different modes of motion can be achieved by changing the DC electric field. Most interestingly, we found a mode of motion that enables the droplets to form a capillary bridge when the electric field is turned on and could break back into droplets states when the electric field is switched off, but only for certain fluids. This repeatable bridge-on-demand behavior using such a simple configuration makes it possible for applications like scalable manufacture of lamenate device for, for example, thermal switches$^{135,136}$. 
4.2 Methods and apparatus

4.2.1 Experimental

Figure 33. Experimental set up of the switchable EHD capillary bridge: The top and bottom aluminum frame is grounded; The top surface of the bottom substrate is connected to a high voltage power supply; the threaded posts are the fine adjustment screws.

Two pieces of 25.4 mm x 25.4 mm x 1 mm ITO glass are used as the substrates for the EHD tests. For both substrates, the ITO surface faces the top where the top ITO is grounded while the bottom ITO is connected to a positive polarity high voltage DC power supply from Acopian (P012HA2.5). The gap size is controlled by a group of 3 fine adjustment screws. The voltage of the high voltage power supply is controlled by a custom LABVIEW code. A CMOS camera is used for measuring the gap size and recording the motion of the liquid with a frame rate of 25 fps. Light from a lamp is projected to a scattering back surface for illumination.
The droplet is cast from a micropipette onto the bottom substrate after a thorough cleaning of the substrates using an excess amount of acetone and isopropyl alcohol. The top substrate, hereinafter referred as the superstrate, is brought down to contact the droplet and raised to break the capillary bridge formed to set the two opposing droplets initial condition. Unless specifically stated, the voltage is turned on from 0 V to the set value in a step function manner and shut off in the same method. The surfaces of the ITOs are modified by using self-assembled monolayers (Gelest (tridecafluoro-1,1,2,2-tetrahydrooctyl)silane) to modify the contact angles. Since these coatings are affected by the heating and cleaning over the course of experiments, so contact angle was also extracted from the droplet videos.

4.2.2 Image Processing

Figure 34. Original images, boundary on the original images, and the extracted boundary for droplets(left) and capillary bridges(right)

The test videos are first cropped into frames. A convolutional neural network is then trained with ~2000 frames of images using Keras for the identification of the
droplets state and the capillary bridge states. Based on the characterization results, different algorithms on the edge detection is applied to extract the binary profiles. Manual addition of points near substrate profiles is conducted to ensure accurate capture of the wetting diameter and contact angle.

4.2.3 Energy and Electric Field Calculation

The total free energy $F$ of the system is calculated by the summation of electrical energy $F_E$, surface energy $F_S$, and gravitational energy $F_G$. The kinetic energy is not taken into account.

$$
\begin{align*}
F &= F_E + F_S + F_G \\
F_E &= F_{Es1} + F_{El}\alpha \\
F_S &= F_{Ss1} + F_{Ss2} + F_l \\
F_G &= \rho g V h_c
\end{align*}
$$

The electric energy is a summation of two parts: $F_{Es1}$, the electrical energy in the top substrate and $F_{El}\alpha$, the electrical energy in the liquid and air.

The voltage drop in the media is approximated using a simplified model as two capacitors in series (Figure 36), with $C_{s1}$ being the superstrate and $C_{l/\alpha}$ being everything between the superstrate and the substrate:

![Figure 35. A simplified model for the voltage calculation](image)

The glass superstrate is assumed to have a dielectric constant of 2.3 and a thickness of 1 mm. The capacitance is calculated to be 13.14 pF. In all phase diagrams in this work, the electric field strength is the electric field strength in the air gap assuming there is no liquid in it.

The surface energy is \( F_s = F_{ss1} + F_{ss2} + F_l \), where the first two terms are the gain of surface energy from wetting on the top and bottom surfaces, i.e. \( F_{ssi} = (\gamma_{lgi} - \gamma_{sgi}) \frac{\pi d_i^2}{4} \) with \( i = 1 \) being the superstrate and \( i = 2 \) being the substrate. The third term \( F_l \) has a form of \( F_l = A_l \gamma \). The side area \( A_l \) is extracted by integrating the boundary of the droplets/capillary bridge, assuming the profile is axisymmetric.

The extracted profile is fed into COMSOL Multiphysics simulation for the calculation of the electric energy and gravitational energy. The physics of electrostatics is selected for the calculation of electric energy. The dielectric constant of the liquid is set to 3.1, and an atmosphere of air is used. The top boundary is set to grounding, and the bottom boundary is set to the corresponding voltage used for the tests. The electrical energy is calculated by

\[
F_{El} = -\frac{1}{2} CV^2
\]

(30)

The \( C \) in equation 30 is the effective capacitance between the top and bottom electrodes, and \( V \) is the voltage between the top and bottom electrodes.
Figure 36. Simulated electric potential for canola (a) pendant droplets and (b) capillary bridge in a parallel plate capacitor.

The gravitational potential energy is calculated by the last equation in equation 29, where the volume and center of mass are calculated by COMSOL using the imported profile.

4.3 Results

4.3.1 Phase Diagram

Figure 37. Phase diagram of 5 μL canola oil. The Bridging, no Debridging case will be abbreviated as B no DB, and the Bridging and Debridging will be abbreviated as B + DB in the rest of the phase diagrams in this dissertation.
By adjusting the voltage and gap size between the substrate and the superstrate, behaviors of specific volumes are plotted onto phase diagrams. The electrical bond number (also referred to as electrocapillary number) here is defined as \( Bo_E = \frac{\varepsilon_0 a E^2}{\gamma} \), characterizing the relative importance of electric force versus the capillary force. The characteristic length \( a \) takes the value of \( a = V^{1/3} \) and the strength of the electrical field \( E \) is approximated by the strength of the electrical field in the air gap. The surface tension of different liquids from literature are used. The slenderness on the y axis is defined by \( \Lambda = H/2a \) where \( H \) is the gap size, is a dimensionless number characterizing how slim the capillary bridge is. As Figure 38, it is pretty obvious that the different phases are scattered in different regions.

By viewing the phenomena of the droplets after turning the electric field on and off from the camera, the droplets are typically classified into five different categories: No movement, jetting, successful bridging and debridging, oscillating, and bridging without debridging. The different behaviors are described as follows:
4.3.2 Successful Bridge and Debridging Process:

4.3.2 (a) Bridging Process

Figure 38. (a), (b) Side view snapshots of the bridging and debridging behavior of B+DB state of a 10.04 µL canola oil in the electric field. The red text means the electric field is off, and the black text means the electric field is on. The 0 s is the first frame after the liquid forming a capillary bridge, and 0 s on the right is the first frame after the capillary bridge breaking back into droplets. The bridging happened at 3.28s in (c)-(h), and the debridging happened at 62.44s in (c)-(h). a-b the liquid’s behavior after electric field’s switching on and off for \(Bo_E = 5.96, \Lambda = 0.22\) (3 kV, 0.96 mm). c, d the characteristic diameters changing during the bridging and debridging process. e,f the contact angle on
the superstrate and substrate during the bridging and debridging process g,h the neck
diameters change during the process of bridging and debridging.

As seen in Figure 39, with the gap size set at 0.96mm, using a voltage of 3kV,
after turning on the electric field, the opposing droplets start to attract each other, moving
the contact line towards the axis (Figure 39c) and shrinking the air gap between them.
With evolution of time, the Taylor cone will jet the liquid towards the opposing droplet.
The jet then merges with the top droplet and develops into a capillary bridge connecting
the substrate and superstrate.

The capillary bridge formed will then see a thickening of its neck. During the
thickening of the bridge neck, convective flow inside the bridge redistribute the mass of
the liquid: When the capillary bridge forms at 3.28 s, the liquid bridge looks symmetric,
while in the next frame (3.32 s), more mass is distributed to the top part of the liquid
bridge and the neck position is shifted downward from the center. This movement stops
at 3.32 s and neck position starts to move back at 3.36 s and this position oscillation
diminishing in magnitude and becomes unrecognizable afterward. With the volume of the
jet provided from the bottom droplet, a broadening of the wetting diameter on the
superstrate is also seen (Figure 39c). The neck width’s change then stayed slow until the
electric field is turned off.

After the bridge forms, the wetting diameter on the substrate keeps shrinking by
up to 26.5% compared with the wetting diameter at 3.28 s. Another phenomenon worth
noticing is the appearance of a thin layer of liquid close to the substrate: this thin layer of
liquid deforms together with the bulk liquid initially, however, with the evolution of time,
the deformation of this layer lags behind the bulk’s and becomes apparent at 0.04 s. This
deformation is slow but not halted. At 4.03 s, this layer becomes indistinguishable by the camera. The formation of this layer might result from the small curvature of this layer as the flow in the system is driven primarily by the surface energy.

During the bridging process, the apparent contact angle experiences an oscillation process while the droplets approach each other. The contact angle on the bottom substrate quickly decreases after the capillary bridge’s formation as the liquid suffers a suction from the bridge. After the thin layer’s disappearing, the liquid bridge shows a higher contact angle than the droplets.

As a summary, in this state, the liquid forms a capillary bridge with smaller footprint on the substrates and higher contact angle with the presence of the electric field.

4.3.2 (b) Debridging Process
When the electric field is turned off, the liquid bridge’s neck thins and breaks back into two droplets. The top droplets then slowly wet the superstrate and substrate, relaxing back into the original two droplet morphology. Comparing with the switching-on process, the relaxation of the liquid takes a longer time.

4.3.3 Description of Other Types of Behavior:
The behavior above is not always guaranteed at other experimental settings. The behavior of the droplets/capillary bridges is influenced by parameters including but not limited to volume, electric field, gap size, contact angle, and liquid properties such as surface tension, density, dielectric constant and electrical conductivity.
As a result, there are other types of typical characteristic behaviors. Of all the liquid tested in this manuscript, the characteristic behaviors are summarized into five categories based on their motion mode recorded by the camera: (1) “No Bridging”: No capillary bridge could form or the liquid bridge formed could not be captured by the camera; (2) “Jetting”: The droplets could jet liquid into the opposing substrate and capture by the camera, but this behavior could not induce a capillary bridge; (3) “Bridging and No Debridging”: Capillary bridge could form by switching on the electric field, but the liquid bridge could not break back into droplets by turning off the electric field; (4) “Bridging and Debridging” by changing electric field: the liquid bridge/droplets morphology change could be switched by electric field in the aforementioned method; (5) “Oscillating”: The liquid bridge – droplets morphology change happens spontaneously at a constant voltage.
Figure 39. Side view images, contact angle, and wetting diameters of 10 µL canola oil in electric field with a B no DB behavior.

4.3.3 (a) Bridging and no Debridging

When the $Bo_e$ further increases, if the gap size is small enough, the two droplets might coalescence and form a capillary bridge between the substrate and the superstrate as described previously. When the gap size is too small, after turning off the electric field, the capillary bridge remains without breaking into droplets. We call this type of behavior “Bridging and No Debridging.” The bridging process is similar to the Bridging and
Debridging phase while when the electric field is turned off, a thinning of the bridge neck and an increase in the contact angle can be observed.

4.3.3 (b) Oscillating

Using the same gap size (0.955 mm) as the Bridging and Debridging phase example and setting the voltage to a lower value (2.75kV) after turning on the electric field, the droplets show the same behavior as the Bridging and Debridging controlled by electric field. However, after the bridge forms, although the voltage is not changed, instability develops and the capillary bridge becomes unstable and breaks back into droplets. If the electric field is not modified, this oscillation behavior will continue.
Figure 40. Side view images, contact angle, and wetting diameters of 10 µL canola oil in electric field with oscillating behavior.

Comparing Figure 41 and Figure 39, we can find the neck diameter formed in this case after the stabilization of the first bridging is smaller than the B+DB case. With the same surface tension and gravitational force, the larger electric forces from the higher electric field stabilized the capillary bridge$^{127}$.

4.3.3 (c) Jetting

Under specific experimental settings, a thin thread of liquid will jet from the Taylor cone formed from one droplet towards the opposing droplet, similar to the initial stage of the bridging process. However, in contrast to the Oscillating phase, the formation
of a jet between the two droplets does not lead to a liquid bridge. This phenomenon is called jetting, or pulsating in other EHD applications such as electrospray. Further decreasing the electrical field, by chance can we observe the jetting behavior, where a small amount of liquid could be observed. Although a frame rate of 25 fps seems to be low to capture the jetting behavior, the periodic relaxation of the droplet after jetting liquid, can typically be observed. This behavior typically happens right after the last no movement point and disappears after the $B_0 E$ is large enough for the liquid to achieve an Oscillating/Bridging and Debridging state. Naturally, a thinner jet results in a larger curvature, making it easier to break before reaching the opposing droplet, preventing the formation of a continuous interface the possible evolution after the formation of a neck. Simultaneously, a thin thread liquid jet could develop a sharp tip, whereas for droplets merging, even if they carry opposite charges, sharp tips could cause quick retaliation of the opposing droplets instead of coalescence.\textsuperscript{139,140} Consequently, jetting behaviors will also be expected to take a larger area of the phase diagram when the slenderness is of larger value.

![Image of jetting behavior](image)

**Figure 41.** The jetting behavior of 5 µL Triton X-100 under 2.5 kV 0.98 mm gap size.

4.4 Discussion:

The problem of the switchable capillary bridge in electric field can be dismantled into several well-studied aspects: (1) tip streaming of charged droplet (2) coalescence of
charged jets/droplets (3) enhanced stability of capillary bridge in electric field and (4) capillary bridge’s stability. This section will analyze these aspects one by one and then summarize them and discuss their role in generating a phase diagram constructed with $Bo_E$ and slenderness $\Lambda$ for different material.

4.4.1 Tip Streaming Process of Charged Droplets

Tip streaming has been a main subject for EHD since more than a century ago\textsuperscript{141}. Recently researchers have gained a better understanding of the phenomena and developed scaling laws for this process. The characteristic field strength is typically set by a value that can make the electrostatic force to balance the surface tension to initiate a jet, i.e.

$$Bo_E = \frac{\varepsilon_0 d_0 E_0^2}{\gamma} \sim 1,$$

where the characteristic length $d_0$ is set by $d_0 = \left(\frac{\varepsilon_0^2 \gamma}{\rho K^2}\right)^{1/3}$.\textsuperscript{142,143} The characteristic time scale for the tip streaming is the capillary time $t_c = \sqrt{\frac{\rho d_0^3}{\gamma}}$.\textsuperscript{22} The general geometry like the wetting radius on the substrate/capillary typically doesn’t play any important role for the local dynamics near the jet. By setting the balance of inertia, axial viscous stresses, electrostatic forces, and surface tension during the last stage of jetting, Ganan-Calvo et al.\textsuperscript{142} calculated the characteristic velocity, jet length, and the tip radius to be:

$$v_z = \varepsilon_r^{-\frac{1}{4}} v_0$$

(31)

$$L_0 = \delta \mu^{-\frac{1}{3}} \varepsilon_r^{-\frac{1}{6}} d_0$$

(32)
\[ R_0 = \varepsilon_r^2 d_0 \] (33)

The \( \delta_{\mu} = \frac{\rho d_0 v_0}{\mu} \) is a dimensionless number similar to the Reynolds number.

The characteristic speed \( v_0 \) is defined by \( v_0 = \frac{d_0}{\tau_e} = \left( \frac{\gamma K}{\rho \varepsilon_0} \right)^{1/3} \)

The kinetic energy of the jet thus can be approximated as:

\[ F_k \sim \rho \pi R^2 L v_z^2 \sim \rho \pi \varepsilon_r^2 d_0^3 v_0^2 \delta_{\mu}^{2/3} \sim \pi \varepsilon_r^2 \rho \delta_{\mu}^{2/3} d_0^3 v_0^2 \mu^{2/3} \] (34)

4.4.2 Coalescence of Charged Droplets

When droplets with opposite charges approaching each other, the coalescence of them is not always guaranteed\(^{139,140}\). The coalescence is determined by the local geometry of the neck formed between the two charged cones. Bird et al., found that critical half angle of the neck region needs to be larger than 59.2°.\(^{139}\)

Assuming a case where two fully developed jets meet each other, the neck half angle can be approximated by

\[ \theta_0 \sim \text{atan} \left( \frac{R_0}{L_0} \right) = \text{atan} \left( \delta_{\mu}^{\frac{1}{3}} \varepsilon_r^{\frac{1}{3}} \right) \] (35)

4.4.3 Axial electric field stabilized capillary bridge

It has been proven for decades that the presence of an axial electric field could greatly enhance the stability of a liquid bridge\(^{144,145}\). The higher the \( Bo_E \), the larger the
critical slenderness$^{146}$. However, the introduction of gravity also influence the stability by a large extent$^{127}$. As will be seen in Figure 44, increasing the electric field could stabilize a bridge from oscillation state to bridge state.
4.4.5 Behavior of Droplets/Capillary Bridge in Electric Field: Roadmap and Phase Diagram

![Flowchart of droplets in DC electric field](image)

**Figure 42.** Flowchart of the droplets in DC electric field
The droplets in the DC electric field is subjected to these processes:

1. A droplet of ~ ul size is cast on the substrate
2. The superstrate is brought down to get in touch with the droplet
3. A capillary bridge forms between the substrate and the superstrate
4. The superstrate is moved up to break the capillary bridge into pendant droplets on the substrate, and the superstrate
5. After waiting for >1min, the electric field is turned on using an electronic switch. The electric field ramps up rapidly using a step function
6. The introduction of the electrocapillary forces starts to change the morphology of the droplets. Based on the magnitude of the electric Bond number they can exhibit different behaviors.
7. As described by Ferrera et. al\textsuperscript{22}, when the electric Bond number is below a critical value, the droplet would form circulational flow inside and oscillate in the axial direction by stretching the apex, on the contrary, while the electric Bond number is above that critical value, the droplets would form transitional flow and eventually jet out smaller droplets given enough room and time, which could be viewed as the cone jet mode of the electrospray. Ganan-Calvo, et al. derived that this critical electric Bond number(electric field strength) based on the balance of jet inertia and surface tension to be \( \sim 1 \).\textsuperscript{142, 147}
8. If the gap size is large enough, the transitional flow will be able to develop into the cone jet mode to eject droplets. As the continuous interface has already been broken after the droplet’s formation, the capillary bridge could not form thus, this can be viewed as the jetting mode. The tip streaming flow has been analyzed by Collins, et
Their work demonstrates that fluid with a longer charge decay time enables longer tip streaming before the emission of the first droplet.

If the gap size is not big enough, then the transitional flow could not have enough room to incept the shedding of droplet from the jet.

If the opposing jet could coalesce, a liquid bridge could form between the pendant droplets. If not, the droplets will jet into each other without forming a bridge. When observed using a low frame rate, the retaliation of the jets is hard to capture so visually it will be captured as the jetting phase.

If the liquid bridge could further develop into a geometry to minimize the surface energy to a value smaller than the droplets state before the turning on of the electric field, the bridge will not be broken after turning off the electric field thus it is a bridge without debridge phase.

When this condition is not met, the bridge formed is an instable or metastable geometry. However, with the electrical energy lowering the total free energy, the total free energy of the bridge state could be lowered, thus making it a favorable geometry in the electric field. This is the desired B+DB state. When the electric field couldn’t provide enough change in the free energy to make the bridge state an energy favorable state, the bridge could not be stabilized and forms the oscillation phase.
4.4.6 Geometric Description and Free Energy Understanding of the Bridging and Debridging Processes

**Figure 43.** Contact angle versus contact radius of 5 μL canola oil for the B no DB, B+DB, and oscillation cases

During the bridge state, the contact radius is smaller than the droplets state, and the contact angle becomes larger. This again confirms our case is different from the typical electrowetting phenomena. The free energy of the three states are also plotted. The free energy is approximated by the summation of electrical energy, gravitational energy and the surface energy as described in the method section. The electrical energy is the relative change compared with the electrical energy of the first frame. The kinetic energy is not represented on these plots as in most cases, the geometry evolution is small.

Although the kinetic energy is neglected, we can get information from the free energy of the “stable states” in electric field (green rectangles in Figure 45). These stable
states are where the profile has evolved after a while after the field is turned on and when the profile does not change much. We will call the two states “deformed droplets” for the droplets prior to the bridging process, and the bridge state after the geometry relaxes after the bridging process. By comparing the stable states in the three phases, we can reach the conclusions below.

To achieve a successful B+DB:

(1) The surface energy of the bridge state needs to be larger than the deformed droplets to provide the driving force to break the liquid bridge after electric field switched off. If this condition is not met, the liquid will fall into the B no DB category.

(2) The free energy of the bridge in electric field needs to be lower than the deformed droplets in electric field to ensure the bridge state in electric field is more stable. If this condition is not fulfilled, the liquid will be in the oscillation state.

The sharp spikes between the droplets in field and the bridge state are from the high surface energy of the slender column and the retracting wetting layer on the substrates during the bridging process. Since we have ignored the kinetic energy, the presence of such a spike acts like an energy barrier between the droplets state and bridge state.

However, the kinetic energy of the tip streaming could reach an order of ~10 nJ from the calculation in 4.3.1(Equation 34). Considering the viscocapillary time of ~ 1ms, without prove, we attribute the energy barrier is surmounted by the viscous dissipation after the coalescence of the opposing jets.
Figure 44. Free energy plots for the 5 µL canola oil for the three states: (a) B no DB (b) B+DB and (c) Oscillation. The electrical energy is subtracted by the initial electrical energy of the system.

4.4.7 Influence of Fluid Volume

The use of large volume means a larger volume to surface ratio. Generally, this is going to make surface forces making smaller influence compared with the volume forces. The only body force involved is the gravitational force since the inertia is not playing an important role except the tip streaming process but the length scale there is not set by the bulk volume. Consequently, Bond number \( Bo = \frac{\rho g a^2}{\gamma} = \frac{\rho g V^{2/3}}{\gamma} \) should be the dominant dimensionless number responsible for the volume change in our case. Increasing volume will make \( Bo \) larger, making the gravity more important in the tests using large volumes. We expect several effects ascribing to the higher \( Bo \).

At the same slenderness (as an example, at a slenderness around 0.18 and 0.21) larger volume requires a higher \( Bo_E \) to move the droplets, but easier to achieve a B+DB
state, indicating the gravity is helping achieve a B+DB state, possibly by providing the instability needed for breaking the capillary bridge formed.

![Graph](image)

**Figure 45.** Phase Diagram of Different Volume Canola Oil: round dots stands for the 5.02 µL, squares for 10.04 µL, and triangles for 15.06 µL.

4.4.8 Phase Diagram: Comparison between Different Materials

Different liquids of divergent properties have been tested using this method to probe the formation of the B+DB phase. The related properties are listed in Table 6, and the derived characteristic values are listed in table 7. Two types of silicone oil with different viscosity are picked for their low electrical conductivity and surface tension. N-Methyl-2-Pyrrolidone (NMP) is picked for its high dielectric constant. Glycerol is selected due to its high dielectric constant and high surface tension. Hexadecane is used
for its slightly higher conductivity. Polyethylene glycol has lower electrical conductivity and higher dielectric constant. 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF4]) is an ionic liquid that has a high conductivity compared with all other materials. Castor oil is applied for its higher viscosity and lower conductivity. A dielectric oil (light naphthenic petroleum distillate) is a lower conductivity material with a lower dielectric constant.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Density $\rho$ (kg/m$^3$)</th>
<th>Dielectric Constant $\varepsilon$</th>
<th>Electrical Conductivity $\sigma$ (S/m)</th>
<th>Surface Tension $\gamma$ (mN/m)</th>
<th>Dynamic Viscosity $\eta$ (Pa*s)</th>
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</thead>
<tbody>
<tr>
<td>Silicone Oil - 5 cSt</td>
<td>918</td>
<td>2.6</td>
<td>1.00E-13</td>
<td>19.7</td>
<td>4.59E-03</td>
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<tr>
<td>Silicone Oil - 350 cSt</td>
<td>970</td>
<td>2.75</td>
<td>1.00E-13</td>
<td>21.1</td>
<td>3.40E-01</td>
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<td>N-Methyl-2-Pyrrolidone (NMP)</td>
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<td>2.00E-08</td>
<td>41</td>
<td>1.65E-03</td>
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<td>Hexadecane</td>
<td>770</td>
<td>2.09</td>
<td>1.00E-07</td>
<td>27.05</td>
<td>2.66E-03</td>
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<td>Glycerol</td>
<td>1258</td>
<td>42.5</td>
<td>6.40E-08</td>
<td>64</td>
<td>1.19E+00</td>
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<td>$\alpha$-Terpineol</td>
<td>934</td>
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<td>1.70E-08</td>
<td>33.2</td>
<td>6.70E-02</td>
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<tr>
<td>Polyethylene Glycol</td>
<td>1128</td>
<td>14.1</td>
<td>1.00E-12</td>
<td>44.1</td>
<td>9.90E-02</td>
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<td>Canola Oil</td>
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<td>3.1</td>
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<td>Castor Oil</td>
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<td>39</td>
<td>8.53E-01</td>
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<td>1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF4])</td>
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<td>14.1658</td>
<td>1.41E-04</td>
<td>48.12</td>
<td>3.38063E-05</td>
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<tr>
<td>Dielectric Oil (Light Naphthenic Petroleum Distillate)</td>
<td>910</td>
<td>2.2</td>
<td>7.50E-12</td>
<td>40</td>
<td>1.82E-02</td>
</tr>
</tbody>
</table>

**Table 6.** Liquids used for the EHD tests and their physical properties
<table>
<thead>
<tr>
<th>Liquid</th>
<th>$d_0$</th>
<th>$t_c$</th>
<th>$E_0$</th>
<th>$E_{0B}$</th>
<th>$v_0$</th>
<th>$R_0$</th>
<th>$F_{K0}$</th>
<th>$\theta_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone Oil - 5 cSt</td>
<td>5.37E-01</td>
<td>8.50E+01</td>
<td>6.57E+04</td>
<td>1.16E+06</td>
<td>1.09E+03</td>
<td>4.99E-03</td>
<td>8.66E-01</td>
<td>5.39E-05</td>
</tr>
<tr>
<td>Silicone Oil - 350 cSt</td>
<td>5.40E-01</td>
<td>8.50E+01</td>
<td>6.78E+04</td>
<td>1.20E+06</td>
<td>7.10E+02</td>
<td>4.99E+03</td>
<td>8.95E-01</td>
<td>4.21E-03</td>
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<tr>
<td>N-Methyl-2-Pyrrolidone (NMP)</td>
<td>1.93E-04</td>
<td>4.25E-04</td>
<td>5.09E+06</td>
<td>1.68E+06</td>
<td>8.49E-06</td>
<td>1.91E-01</td>
<td>1.10E-03</td>
<td>1.19E-09</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>6.33E-05</td>
<td>8.50E+01</td>
<td>7.09E+06</td>
<td>1.36E+06</td>
<td>5.57E-06</td>
<td>6.20E-01</td>
<td>9.15E-05</td>
<td>4.33E-11</td>
</tr>
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<td>Glycerol</td>
<td>9.65E-05</td>
<td>1.33E-04</td>
<td>8.84E+06</td>
<td>2.19E+06</td>
<td>3.32E-03</td>
<td>2.84E-01</td>
<td>6.29E-04</td>
<td>4.20E-07</td>
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<td>α-Terpineol</td>
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<td>5.00E-04</td>
<td>4.34E+06</td>
<td>1.51E+06</td>
<td>2.24E-04</td>
<td>3.20E-01</td>
<td>3.47E-04</td>
<td>8.10E-09</td>
</tr>
<tr>
<td>Polyethylene Glycol</td>
<td>1.41E-01</td>
<td>8.50E+00</td>
<td>1.92E+05</td>
<td>1.74E+06</td>
<td>1.02E-02</td>
<td>8.58E-03</td>
<td>5.31E-01</td>
<td>7.52E-04</td>
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<td>Canola Oil</td>
<td>2.22E-04</td>
<td>5.67E-04</td>
<td>4.07E+06</td>
<td>1.47E+06</td>
<td>1.70E-04</td>
<td>2.96E-01</td>
<td>3.92E-04</td>
<td>6.54E-09</td>
</tr>
<tr>
<td>Castor Oil</td>
<td>9.02E-02</td>
<td>4.25E+00</td>
<td>2.28E+05</td>
<td>1.64E+06</td>
<td>6.12E-02</td>
<td>1.45E-02</td>
<td>1.93E-01</td>
<td>1.45E-03</td>
</tr>
<tr>
<td>1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF4])</td>
<td>5.15E-07</td>
<td>6.03E-08</td>
<td>1.05E+08</td>
<td>1.82E+06</td>
<td>5.99E-09</td>
<td>4.40E+00</td>
<td>1.94E-06</td>
<td>1.75E-15</td>
</tr>
<tr>
<td>Dielectric Oil (Light Naphthenic Petroleum Distillate)</td>
<td>3.84E-02</td>
<td>1.13E+00</td>
<td>3.50E+05</td>
<td>1.66E+06</td>
<td>7.20E-04</td>
<td>2.78E-02</td>
<td>5.69E-02</td>
<td>5.15E-06</td>
</tr>
</tbody>
</table>

**Table 7.** Characteristic properties for selected EHD liquid. Values in bold denote the unfavorable property for jet coalescence.

The $d_0$, $t_c$ are the characteristic length for the streaming jet and the local capillary time as defined in section 4.3.1. The local characteristic field strength $E_0$ is calculated by setting the local $B_0E = \frac{\epsilon_0E_0^2}{\gamma d_0}$ to be 1 and the bulk field strength $E_{0B}$ is calculated by using the bulk characteristic length $a = V^{1/3}$ for this relation assuming a volume of $\sim 5 \mu L L_0$, $v_0$, $R_0$, $F_{K0}$, and $\theta_0$ are the characteristic jet length, jet tip length, jet front radius, kinetic energy of the jet, and the approximated half cone angle of a fully developed jet.

From Table 7, we can see different materials have different failure modes based on the geometry and electric field limit of the device (~mm gap size, electric field strength ~ kV/mm):
(1) The characteristic time for the two types of silicone oil tested is too long; thus their motion is not significant. In addition, the local field strength during the tip streaming process is well below the bulk field strength, meaning that the field required for forming the jet is even smaller than the field required to move the bulk liquid. This oversupply of voltage/field might turn the tip streaming into a multi-jet electrospray mode.\textsuperscript{149, 150}

(2) For hexadecane and NMP, due to the small jet length, we would expect the jetting mode to be the main mode at a higher slenderness.

(3) Glycerol and PEG are able to form a slender cone jet that is long enough to make a stable neck region between opposing droplets. As seen in Figure 47, both liquids could form a stable bridge at a slenderness larger than 0.34.

(4) The cone angle of the jet for $\alpha$-Terpeniol is smaller than the critical value (59.3°); thus even if the jets could meet, it could not develop into a stable bridge.

(5) Despite canola oil has an approximate half cone angle close to the critical value (59.3°), with a gap size slightly smaller than the sum of the length of the jets, it is possible to meet the condition for a locally stable neck.
Figure 46. Phase diagram for different material with $Bo_E$ being the electrical Bond number and $\Lambda$ being the slenderness.

Additional tests were carried out on liquids with similar molecular structure as canola oil (Figure 47). For the short-chain triglyceride, as its properties are quite different from the ones of canola oil, a different phase diagram shows up as expected: no B+DB is observed and when the electric field is high, the liquid shows an oscillating behavior. With a longer chain length, the glycerol tricaprylate starts to show an area of B+DB. Using an even longer chain length molecule requires a higher $Bo_E$ to generate motion of the droplet under the same slenderness but enables the B+DB behavior at a lower
slenderness.

Figure 47. Phase Diagram of Different Triglyceride, with circles showing the behavior of glycercyl triacetate, squares showing glycerol tricaprylate and triangles showing the glycercyl trioleate.

4.5 Conclusions

By placing 5 µL ~ 15 µL liquid material of different types in a parallel plate capacitor with a dielectric layer, we have found four types of characteristic behavior modes of the liquid subjected to an axial direction DC electric field. Through specific combination of material properties, an electric field controlled switchable B+DB mode has been found at intermediate gap size for liquid with several leaky dielectric materials. A small contact angle, the ability to form a tip streaming cone jet, and the coalescence of opposing jets are critical for the liquid media selected. By analyzing the free energy, we
found for the materials that could achieve this behavior, the key point in achieving this state is to have a capillary bridge with higher surface energy than the droplets state and an electric field that makes the total free energy lower during the bridge state.

5. Outlook and Future Directions

5.1 Utilizing the Fast Heating and Cooling of Laser Heating.

As seen in section 2.2.2, the heating and cooling rate of FLaSk annealing could reach a value $> 10^7 K/s$. With the fast heating/cooling rate, FLaSk annealing can be used for systems that require fast heating/cooling, such as the probing of optimal glass formation ability of BMG\textsuperscript{29}. With FEM thermal simulation, the cooling rate at critical temperature could be probed easily. With the aid of other surface examination methods, including XRD, SEM, or even optical microscopy, the critical cooling rate for BMG could be probed. Figure 48 shows how the thermal history of a UHS subjected to ~ mm spot size laser shot with different pulse width, spot size, and fluence.
Figure 48. In Submission work in collaboration with Liu, N. et. al. (a) Schematics of Single Pulse Laser Annealing. Laser beam (red) passes transparent sapphire substrate (light gray) and heats tungsten absorption layer ((i) and (ii)). Heat generated from absorption layer then dissipates across a 10 nm dielectric layer and melt the thin film sample (iii). After Laser beam is turned off, system is cooled down by natural cooling through sapphire substrate, and thin film sample solidifies (iv). (b) in Single Pulse Laser Annealing, thermal profile is controlled by varying the duration time of the laser pulse. Thermal simulation of two laser pulses with duration time of 0.1 ms (orange) and 1 ms (yellow) are shown with significant varied cooling rate (R1 and R2). (c) By changing the
laser pulse duration time, from 0.1 ms to 10 s, cooling rates ranging from 106 to 103 K/s can be realized. Error bar is defined by cooling rates at temperatures between 500 K and 800 K, which is the typical region of the nose temperature of TTT diagram for most glass forming alloys. (d) Simulated result of laser heating/cooling profile with different laser duration time: (i) 0.1 ms, (ii) 1 ms, (iii) 10 ms, and (iv) 100 ms, showing cooling rates controlled over orders of magnitude. (e) High-throughput measurement on material library. Sputtered material library is meshed into ~200 different compositions. (f) Four different laser pulses are applied to each composition, giving cooling rates varying through 4 orders of magnitude.

The use of FLaSk annealing on BMG system, in addition to the extreme heating and cooling rate, could provide additional convenience: BMG as a glassy system, could exhibit similar behavior while subjected to thermocapillary dewetting. Figure 49 shows a BMG deposited on heating substrate showing multiple characteristic behaviors at different heating conditions: smoothing, delamination, thermocapillary dewetting, possible melting and crystallization. Additionally, analyzing the feature size evolution might provide additional information as the crystallization might lower the potential
energy thus hindering the growth of dewetted features.

Figure 49. FLaSk dewetting of an Au-Si-Al BMG glass deposited on UHS with different power and exposure time

5.2 Possible Improvements on FLaSk Annealing Process:

By installation of a high-speed camera focusing on the material deposited on the UHS, in-line real-time examination of the material properties could be conducted. This could further reduce the required testing area from arrays of features to lines of features.

Due to the inhomogeneity introduced by the manufacture process of the heating substrate and the inaccuracy of the focusing process, the thermal profile created by FLaSk heating could introduce great error. Thus it is favorable to conduct a more direct temperature
measurement of the local temperature. This can be done by relating temperature related phenomenon including photoluminescence\textsuperscript{151, 152}, and temperature dependent optical properties like the reflectance\textsuperscript{153, 154}.

5.3 EHD Capillary Bridge Thermal Switch for Pyroelectric Waste Heat Harvest

Pyroelectric waste heat harvest device has high efficiency but it has to rely on an oscillating thermal field owing to the working mechanism: Olsen cycle. Olsen cycle is the optimized thermodynamic cycle employed for regenerative pyroelectric energy converter that takes advantage of the temperature dependent charge(electric displacement)-electric field hysteresis(Figure 51 a) of pyroelectric materials(a subset of ferroelectric material).\textsuperscript{155} The Olsen cycle involves four processes: 1-2, isothermal charging; 2-3, iso-electric field heating; 3-4, isothermal discharging and 4-1, iso-electric field cooling (Figure 51 b).\textsuperscript{156}

As Olsen cycle requires a large electric field across the pyroelectric material, using a voltage controlled thermal switch could minimize the efforts for synchronizing the thermal and electric field simply by adding a transistor circuit. The EHD CB thermal switch thus could help achieve this goal: raising the electric field turns on the capillary bridge and reduces the thermal resistance between the heater and the pyroelectric material, heating up the pyroelectric material. These processes constitute step 1-2 and 2-3 in the cycle diagram. Lowering the electric field breaks the capillary bridge, thus makes the pyroelectric material to cool down in a lower field. This cooling process thus help achieve the step 3-4 and 4-1, concluding an Olsen cycle.
Figure 50. Olsen cycle for pyroelectric cycles. (a) Ferroelectric charge-voltage hysteresis for Pb$_{0.99}$Nb$_{0.02}$(Zr$_{0.68}$Sn$_{0.25}$Ti$_{0.07}$)$_{0.98}$O$_3$ at different temperature. Reprinted from R. Olsen, et al., Journal of Applied Physics (1983)$^{155}$, with the permission of AIP Publishing, copyright(1983) (b) Displacement-electric field diagram for an Olsen cycle. Reprinted from F. Lee, et al., Applied Thermal Engineering (2012)$^{156}$, with permission from Elsevier, copyright(2012) (c) Schematic drawing for a EHD CB thermal switch, the numbers on the drawing corresponds to the processes in (b)
Figure 51. (a) Sawyer-Tower circuit for pyroelectric device characterization. (b) Schematic drawing of the EHD capillary bridge thermal switch with pyroelectric device (c) a top view of the 3 x 3 5µL castor oil droplets cast on a sapphire substrate coated with aluminum (d,e) The charge – field phase diagram and temperature on the back of the bottom sapphire substrate for system running without the EHD capillary bridge thermal switch as a blank comparison ran at 0.02 Hz, 0.5 duty cycle. The high voltage and low voltage for the PZT-5H are -500V and -400V. The top aluminum frame is heated to 80°C controlled by a custom PID controller built by LABVIEW. The temperature in (e) and (g) are the temperature monitored by an infrared thermal camera. The monitored area is the center ~ 1 cm × 1 cm of the back of the bottom sapphire. (f,g) The charge – field phase diagram (f) and temperature (g) on the back of the bottom sapphire substrate for system running with the EHD capillary bridge thermal switch

A demo EHD CB thermal switch device has been made using a 3×3 5 µL castor oil droplet array. With a heat source set at 80 °C and running the device at 0.02 Hz, a
power density at $12.15 \, W/m^3$ is reached. Further improvements have to be made to optimize efficiency.

5.4 Convective Heat Transfer in EHD Capillary Bridge Thermal Switch: Enhanced Thermal Behavior

![Graph](image)

**Figure 52.** The max temperature on the back surface of a 1 mm thick ITO glass substrate while during the first bridging process of a 5 µL pure canola oil droplet vs. a 5 µL canola oil doped with 1.82% graphene 32.7% BaTiO$_3$ 0.34% Brij30. All concentrations are in weight percentage. 0 s is when the capillary bridge is established.

Liquid material other than liquid metal typically has a low thermal conductivity compared with solid material. Efforts have been made to dope liquid material with high conductivity nano materials to make nanofluid to enhance the heat transfer properties. However, it is also generally accepted that the increasing volume ratio of nanoparticles typically brings a side effect of higher viscosity. The heat transfer thus suffers a tradeoff between the increased thermal conductivity and the lowered heat transfer coefficient from the suppressed convection. In our case, we made a nanofluid using graphene, BaTiO$_3$
nanoparticles and a surfactant Brij 30. Although the thermal conductivity is doubled for the nanofluid, the performance of the pure canola oil outpaced the nanofluid’s as indicated by the max temperature change during the first bridging process (Figure 52).

![Image]

**Figure 53.** (a) IR image of an EHD-CB thermal switch during on state: 3.5 kV, 1 mm gap size. The color bar shows the temperature. (b) The pixel value of a fixed point on the capillary bridge during the on state.

By analyzing the pixel value’s oscillation of a fixed point on a capillary bridge, we get an approximate velocity of the convection in a pure canola oil droplet to be ~ 1 mm/s. The Peclet number is approximated as:

\[ Pe = \frac{vl}{\alpha} \sim 10 \]  

indicating the convective heat transfer is playing a larger role than the conduction process.

While trying to achieve the EHD switching using nanofluid of canola oil and barium titanate particles, we found due to the large electric field and the difference in the dielectric constant, electrophoretic deposition of nanoparticle suspension could happen.
The electrophoresis deposited the barium titanate particle on one of the substrates and forms a sub-mm size cone with higher thermal diffusivity. The cone deposited could further work as a fin to enhance the heat transfer. Simultaneously, the depletion of particles lowers the suspension’s viscosity to enhance the convective heat transfer. However, the change of substrate from a smooth plane surface to a surface with a rough cone might complicate the switching behavior thus this approach worths further investigation.

**Figure 54.** (a-e) 7.5 uL of canola oil with 1 wt% 400 nm barium titanate nanoparticles subjected to manually applied 2.95 kV field to bridge and debridge a 4.62 mm gap. Grid size is 1 mm. (f) Side view during the first bridging (left) and after final debridging (right).
6. Summary

This dissertation has looked into three objects in the micro/nano manufacturing field involving the modification of surface force to achieve synthesis, metrology and design of viable structure for the scalable manufacture and inspection of functional thin film material/device:

Chapter 2 introduced FLaSk dewetting of gold nano film on meltable glass substrate and a localized physical vapor deposition (LILPVD) through elongated dwelling time of gold melt from the trapping of the underneath meltable substrate. The laser annealing parameters including NA, power, scanning distance are investigated. A comparison test is done on fused quartz substrate that doesn’t soften during the process. LILPVD as a localized nanoparticle deposition technique is demonstrated by patterning a seeding layer for ZnO nano rod growth.

Chapter 3 used FLaSk thermocapillary dewetting of glassy thin films with different molecular weight, film thickness. It has demonstrated how to use thermal gradient and an optical microscope to achieve the analysis of the rheological properties of supported glassy thin films. It has shown its ability to probe the difference in the film’s rheological property from multiple influencing factors.

Chapter 4 designed an electric field controlled EHD capillary bridge oscillator that can be used as a thermal switch and possibly other transport applications. The mechanism is analyzed through free energy and geometrical analysis. Phase diagrams for possible working fluids are developed.
Chapter 5 gives a brief outlook on the possible improvement of these projects and has shown the preliminary results of applying the EHD capillary bridge oscillator as a thermal switch in a scalable pyroelectric waste heat harvest device.

7. References


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