

Nanoscale pattern formation from laser induced thin film instabilities: Role of internal and external effects

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Dedication

This dissertation is dedicated in loving memory of my father, who enlightened me with his philosophies on life and instilled the importance of hard work and higher education

Sankar Naidu Yadavali (1960-2014)

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To my mother, who taught me to face problems & unknown fears courageously in life and to stay humble and simple

Mrs. Padmavathi Yadavali

&

To Prashasti, for the unconditional love, being supportive, patient, understanding and making my life more fun and colorful

&

Lastly, to all the wonderful people who work hard to create a new world in which people may learn to live in harmony with each other as well as in harmony with nature

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अज्ञानतिमिरान्धस्य ज्ञानाञ्जनशालाकया ।
चक्षुरुन्मीलितं येन तस्मै श्रीगुरवे नमः ॥३॥

Salutations to the Guru, who Removes the Darkness of Ignorance from our Blind (Inner) Eyes by applying the Collyrium of the Light of Knowledge I

By Whom our (Inner) Eyes are Opened; Salutations to that Guru ॥

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Abstract

Pulsed laser assisted pattern formation in single and bilayer metal films was investigated in this dissertation. The overall goals were: (1) to overcome limitations in conventional pulsed laser dewetting techniques, (2) to better understand the role of effects such as thermal gradients, dispersion forces, pressure gradients, and electric fields on pattern formation, and (3) to investigate nanostructure morphology and its progression in the dewetting of bilayer metal films. This study was divided into two parts. In the first part, pulsed laser-induced instabilities of single layer metal films was discussed. The spinodal dewetting of Au films, a novel Rayleigh-Taylor instability induced by pressure gradients, and the role of DC electric field on pattern formation is presented. In pulsed laser dewetting of Au, the trend in particle spacing and diameter was consistent with the predictions of classical spinodal dewetting theory. The early stage dewetting morphology changed from bicontinuous structures to hole like, and thermal gradient forces were found to be significantly weaker than dispersive forces in Au. Next, we showed through experiment and theory that nanoscale Rayleigh-Taylor instabilities can be seen in thin metal films. This instability was a result of pressure gradients developed when Au films were melted inside a bulk fluid like glycerol. One of the primary findings in this pattern formation was that the spacing of the nanoparticles was independent of the film thickness and could be tuned by the magnitude of the pressure gradients. Finally, we concluded this part by presenting the discovery of phase array self assembly of metallic nanoparticles under the application of a DC electric (E) field. In the second part, the morphology evolution under pulsed laser dewetting of a bilayer of the immiscible metals Ag and Co was investigated. We found multiple transitions in morphology for bilayers and correlated these transitions with an experimentally constructed dewetting morphology phase diagram. Finally, the role of thermal gradients was assessed in the formation of a variety of bimetal nanostructure. Work by our collaborator using computational non-linear dynamics showed that different nanoscale morphologies such as core-shell, embedded, or stacked cases could be formed in the Co-Ag system.

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Chapter 1

Introduction

The overall goal of this thesis is to research new ways to synthesize metallic nanoparticles on a surface and is motivated fundamentally by the interesting behaviors demonstrated by fluid thin films and droplets when exposed to external fields, such as thermal transients and electric fields.

From the viewpoint of the broader scope of this thesis research, the goal is to make impact in the area of nanomaterial synthesis. Nanoscale materials often shown new and/or different properties compared to macroscopic bulk materials and individual atoms/molecules. One area of nanoscience research has been a fundamental study of the physical property of materials using cutting-edge experimental and theoretical tools to understand structures in the nanometer scale. The ultimate goal of this line of work is to develop materials and devices that will overcome the existing technological limitations and even create new and novel functionalities. Concurrent with this research, the development of synthesis techniques that are able to manipulate and arrange matter on the nanometer level such that useful nanomaterials identified above can be turned into real applications with enhanced optical [1], plasmonic [2, 3], magnetic[4], and magneto-plasmonic properties is another critical area of research.

As developed by Gustav Mie in 1908, spherical metallic nanoparticles with frequency-dependent dielectric function $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ (where ϵ' and ϵ'' are the real and imaginary parts), embedded in a host dielectric medium ϵ_h show an extinction cross-section σ_{ext} given as:

$$\sigma_{ext} = \frac{24\pi^2\epsilon_h^{3/2}d^3}{\lambda} \frac{\epsilon''(\omega)}{[\epsilon'(\omega) + 2\epsilon_h]^2 + \epsilon''(\omega)^2} \quad (1.1)$$

where d is the diameter of the particle, and λ is the wavelength of incident light. Since many metals possess a negative value of $\epsilon'(\omega)$, it is widely recognized that the plasmon resonance occurs at the frequency ω_{lsp} when the extinction cross-section σ_{ext} is maximized, i.e. when the condition $\epsilon'(\omega) = -2\epsilon_h$ is met. From Eq. 1.1, the principle of plasmon sensing utilized in detecting biomolecules or chemicals with high sensitivity can be very simply described. When an localized surface plasmon resonance (LSPR) substrate, i.e. a surface with plasmonic nanostructures, such as that shown in Fig. 1.1(a), is exposed to ambients with different refractive index, the position of the LSPR wavelength (frequency) is shifted Fig. 1.2(A) in

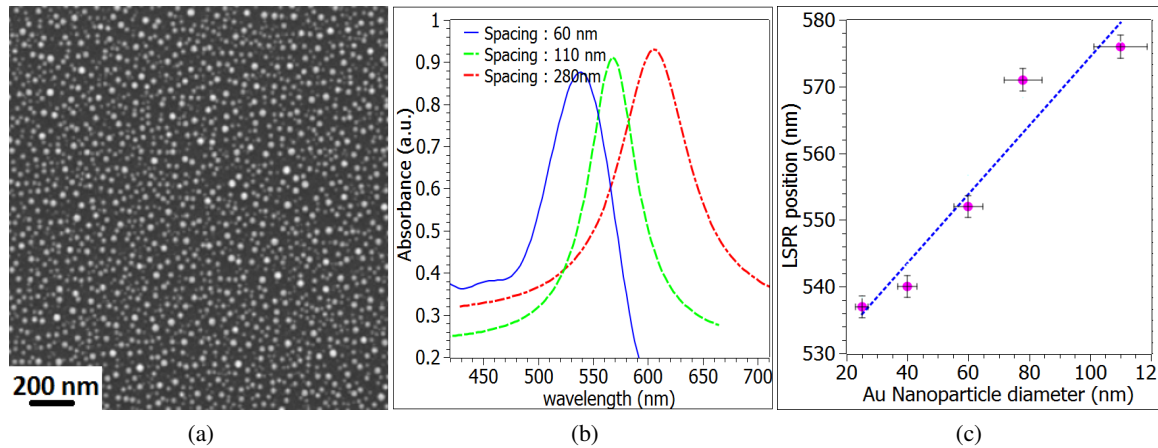


Figure 1.1: (a) SEM image of Au nanoparticles on sapphire substrate with mean diameter of 38 nm (b) LSPR position as a function of spacing between Au nanoparticles on Quartz substrate. (c) LSPR position as a function of Au nanoparticle diameters. Data from [5].

accordance with the resonance condition $\epsilon'(\omega) = -2\epsilon_m(\omega)$, i.e. a color change occurs. This idea makes it an extremely simple technique, and has been utilized to detect trace amounts of chemicals such as anthrax bacteria [7] and trinitrotoluene (TNT) [8], as well as to monitor biochemical processes [9, 10, 8, 11].

The challenge that exists in this field is to be able to optimize the performance of the sensing by manipulating the characteristics of the nanostructures that control plasmon behavior. For example, as shown by Farzinpour et al [5] in Fig. 1.1(b,c), changing size and spacing of nanoparticles changes the LSPR wavelength location. This can have implications to sensitivity, as shown by the work of Haes et al [6] and depicted in Fig. 1.2. LSPR wavelength of Silver nanoparticles are tuned by varying their diameters and then used for chemical sensing. They showed that when magnesium(II) molecule is adsorbed on Silver nanoparticles having LSPR wavelengths both near and far from a molecular resonance in Mg(II), the resulting LSPR shift is quite different (Fig. 1.2(A)). When the LSPR position is close to the molecular resonance, the shift is either enhanced Fig. 1.2(B) or suppressed Fig. 1.2(D). In contrast, when the LSPR position is far from the molecular resonance, the shift is less dramatic Fig. 1.2(C) and closer to expectations based on a simple refractive-index change.

Likewise, there are many other applications of nanoparticles (NPs) arranged on a surface where the control of the NP characteristics is an extremely important requirement of any synthesis routes. This includes fields such as catalysis, magnetism, Surface Enhanced Raman Sensing (SERS). *Therefore, the focus of the research to be performed in this dissertation is to explore robust and cost effective pathways to synthesis nanostructures of well defined size, shape, morphology, and spacing on a surface.*

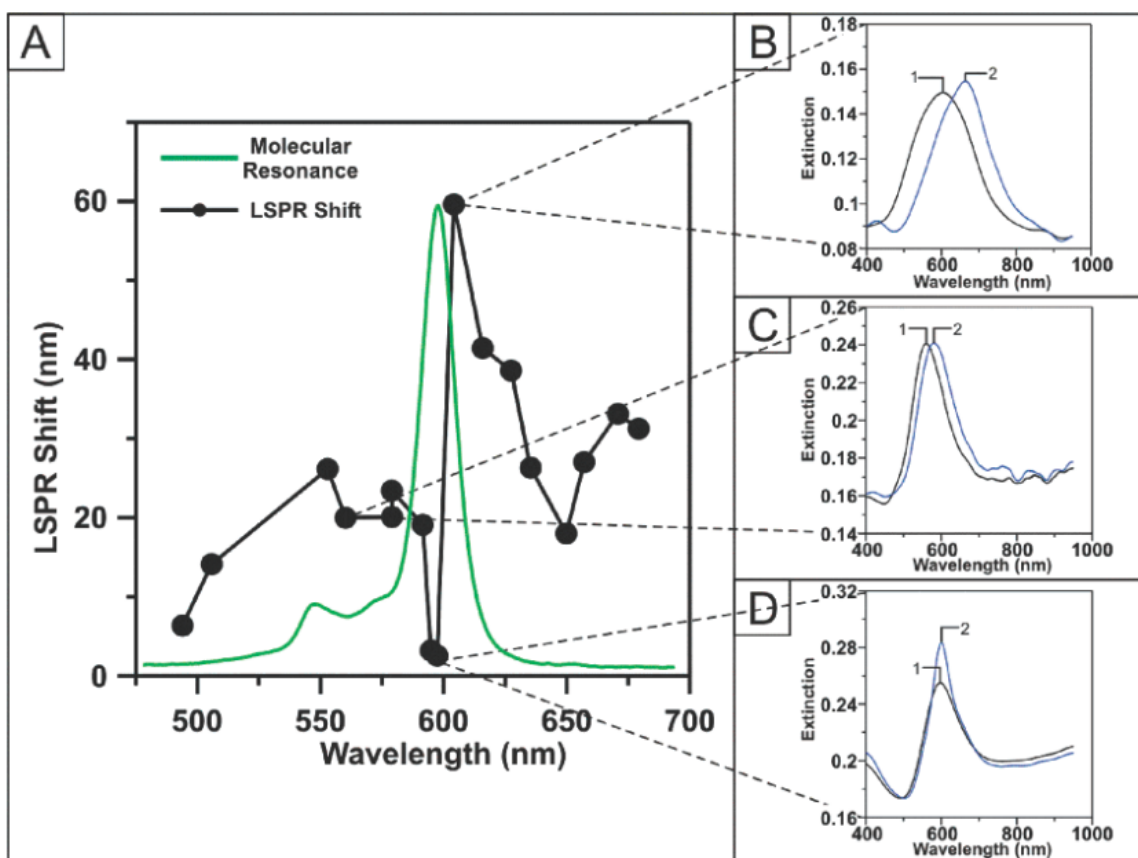


Figure 1.2: (a) LSPR shift induced by magnesium(II) adsorption on Ag nanoparticles versus initial nanoparticle LSPR wavelength (black dots). The absorption spectrum of magnesium is shown in green color. (B-D) LSPR spectra before and after magnesium adsorption. Measured LSPR shifts are (B) 60 nm (C) 20 nm (D) 2.5 nm. (b) Size and Shape dependence of LSPR for Silver Nanoparticles. Data from [6]

1.1 Literature Review: Synthesis of nanoparticles on surfaces: Current State of Art to make nanostructures.

In this section, we review the current state of art with particular attention paid to techniques that can synthesize nanoparticles on a surface. The most important ones are summarized in Table (1) under two categories based on their fundamental methodologies. Self-organization and self-assembly routes generally refer to spontaneous organized pattern formation as a consequence of the system approaching equilibrium by reducing its free energy. Lithography generally refers to the ability to define patterns on surfaces by using resists and masks.

Table 1.1: Typical synthesis and patterning methods used to fabricate nanostructures on a surface

#	Self-Organization/Self-assembly	Lithography
1.	Thermal Annealing	Conventional lithography
2.	Chemical Synthesis	Soft lithography
3.	E-beam/Ion beam	Nanosphere lithography
4.	Pulsed Laser Synthesis	Others
5	LIPSS	

1.1.1 Lithography

1.1.1.1 Conventional Lithography

The lithographic techniques are classified as either “parallel writing” or “sequential writing”. In parallel writing techniques, the entire pattern is fabricated simultaneously using a mask which dictates the features to be reproduced. For example, in an optical lithography, a photosensitive material on substrate is selectively exposed by a radiation source such as light using a mask. The photo resist is placed in a developer solution, it will etch away one of the two regions either exposed or unexposed, the remaining patterns are then used as templates for nano fabrication[12, 13]. In parallel writing methods, the final resolution of the pattern is limited by the wavelength of the light used. The use of shorter wavelengths like UV and soft X-ray allows a reduction in feature size, but these process brings increasing technical difficulty. Alternative techniques like sequential lithography have been developed to overcome limitations in parallel writing. In sequential writing techniques like electron or ion beam, the pattern is written point by point on the resist surface through a computer controlled program where the mask pattern is defined. Under ideal conditions, it is possible to reach sub-10 nm resolution.

Each of these conventional Lithographic fabrication tools are commercially available and are the major technological driver for the past few decades particularly in microelectronics industry. The advantage of these technique are that very high resolution patterning with resolutions of sub-micron and nanometer scale is possible. However, the generic challenges associated with lithography includes mask technology, development of appropriate resist materials and overall the state of the art lithography system costs tens of millions of dollars as shown in Fig. 1.3. Hence, the cost of purchase and maintaining the tools often limits their availability to carry out research activities in many laboratories.

Comparison of primary nanolithography techniques. Note that all numbers quoted are approximate and highly configuration/application dependent						
Technique	Optical	E-Beam (Direct Write)	E-Beam (Projection)	Focused Ion Beam	EUV	Nano- Imprint
Resolution (nm)	100	20	50	30	30	10
Alignment (nm) ^a	30	10	20	10	10	100
Throughput (Feature/s) ^b	10 ¹⁰	10 ⁴	10 ¹⁰	10 ¹ –10 ²	10 ¹¹	10 ¹²
Instrument Cost (\$) ^c	10 ⁷	10 ⁶	10 ⁷	10 ⁶	5 × 10 ⁷ ?	10 ⁵

Figure 1.3: Comparison of Lithographic techniques. Data table was taken from reference[14]

1.1.1.2 Soft Lithography

Soft lithography is one of the many lithographic and patterning techniques proposed to overcome the disadvantages in conventional lithography techniques. The concept of soft lithography was introduced by Whiteside's group at Harvard [15] in 1988. It uses a soft mold prepared by casting a liquid polymer precursor like polyurethanes, epoxides and polyamides against a rigid master like Silicon. The master is fabricated via a conventional lithographic method. For example, a PDMS mold is fabricated by pouring its liquid precursor over a lithographically made Silicon master, cured to induce cross linking, and then peeled off. The PDMS mold can then be used as a mask, stamp or mold for generating or replicating structures. The resolution limit in soft lithography is determined by van der Waals, wetting and kinetic factors, and not by the optical diffraction limit [16, 17]. Unlike conventional lithography techniques that must take place in a clean-room facility, soft lithography can be carried out by hand in an ordinary laboratory. Soft lithography can produce nanostructures of complex organic molecules needed for biological studies, can print or mold pattern on curved or planar surfaces. One of the main beneficiaries of soft lithography is the field of microfluidics which relies on rapid prototyping of PDMS devices. But this technique is not ideal to fabricate complex nanostructures and nanoparticles on substrates.

1.1.1.3 Nanosphere lithography

Nanosphere lithography is a promising inexpensive tool to fabricate nanostructures on surfaces. The technique is a multi step process and relies on the self assembly of polystyrene beads on substrates. In the first step, a flat substrate is coated with a suspension containing monodisperse spherical polystyrene colloids and left to dry. The drying or evaporation of the solvent induces the formation of a meniscus between the particles and therefore leading to attractive capillary forces which give rise to self-assembly of particles[18, 19]. Depending on the surface properties and electrolytes used in the colloid suspension, the nanosphere will self-assemble into a hexagonal close packed monolayer or bilayer. The assembled monolayer or bilayer is then used as a mask to selectively pattern the substrate. The material of interest can be

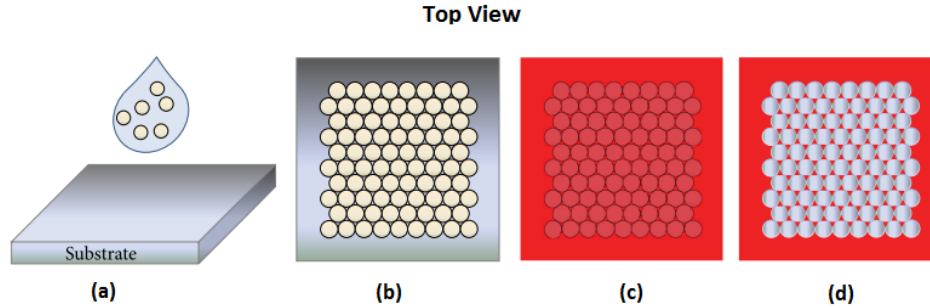


Figure 1.4: (a) Cleaning of the substrate and deposition of the colloidal suspension. (b) Self-organization of polystyrene beads on the substrate. (c) Deposition of the desired material. (d) Removal of the polystyrene beads (lift off). Image from Ref. [18]

deposited through the interstices of the ordered polystyrene beads. The mask can be removed by sonication in an adequate solvent solution. The disadvantages of this techniques are: it is a multi step process and at present only hexagonal geometry of nanoparticles can be obtained. The details are shown in the schematic in Fig.1.4.

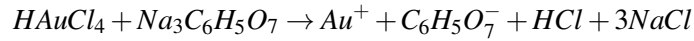
1.1.1.4 Others

Other lithographic techniques include Scanning probe lithography, Colloidal lithography, and flash imprint lithography. Scanning probe lithography uses the tip of a scanning probe microscope like atomic force microscope (AFM) and scanning tunneling microscope (STM) to selectively remove certain areas on a surface or to deposit material on a surface with nanometer resolution. The main advantage of this technique is the high resolution capability and ability to generate patters with arbitrary geometries. However, the limited throughput of scanning lithography techniques has thus far prevented its implementation in industrial scale applications. A recent review on these techniques can be found in Nature nanotechnology by Richardo Garcai et. al [20]. In Colloidal lithography, a similar concept to nanosphere lithography is used by applying a colloid suspension as a mask for the fabrication of nanostructures on surfaces. In this technique, the short range electrostatic forces are employed to obtain short range ordered arrays of nanospheres on a substrate [21]. In flash imprint lithography, conventional optical lithography is used to etch patterns on a quartz substrate. The quartz substrate is then used as a rigid master, it is pressed against a thin film of liquid polymer, which fills the master recesses [22, 23]. Exposing to ultraviolet light source solidifies the polymer to create the desired replication.

1.1.2 Self-organization/ Self-assembly

1.1.2.1 Chemical Synthesis

Chemical synthesis of nanoparticles in solutions is generally a simple and inexpensive way to make materials. A variety of sizes and shapes with monomodal size distribution can be synthesized [24]. As an example, the synthesis of Au nanoparticles by chemical methods is achieved by a chemical reaction such as the reduction of chloroauric acid ($HAuCl_4$) with trisodium citrate ($Na_3C_6H_5O_7$) as shown below:



The amount and concentration of citrate used controls the diameter of gold nanoparticles [25]. The Au nanoparticles in solution can be stabilized by repulsive coulombic interactions or by using some other capping molecules. In a similar manner Ag, Cu and other metal nanoparticles can be synthesized. However when the solution is dispersed on substrates, there is no control over the nanoparticle spacing and the mechanical adhesion of particles on substrates is very weak. This leads to poor reusability of nanoparticles on substrate and poor reproducibility of morphologies.

1.1.2.2 Thermal Annealing

Solid films are usually metastable or unstable in the as-deposited state, and they will dewet or agglomerate to form islands when annealed to sufficiently high temperatures. This process is driven by surface energy minimization and can occur via surface diffusion well below a film's melting temperature [26, 27]. Self Organization (SO) via thermal annealing is largely driven by the relative ease with which nanostructures can be fabricated over large areas, and are typically produced in a few hours at temperatures well below the melting point of the metal, and can be achieved using simple instrumentation such as a sputter coater to make the thin film and a tube furnace to anneal. This process, commonly referred to as solid state dewetting, is typically initiated at holes in the film which extend through the film to the substrate surface. Such holes typically occur at grain boundary triple junctions [28] which are randomly arranged in the film. As a result, the size, size distribution and spacing of the ensuing nanostructures cannot be well controlled [29].

1.1.2.3 Dewetting under energetic particle beams

Thin metal films self organize into nanostructures when irradiated with energetic beams such as electron and or ion beams. The thermal energy required for the self organization is provided by the particle beam with the advantage that, since the beam diameter is of order of 10 to 20 μm , pattern formation can be achieved locally and/or at specific areas of interest on the sample surface. One of the disadvantages of this approach is that it is difficult to scale it up to very large areas [30, 31].

1.1.2.4 Laser induced periodic surface structures (LIPSS)

Irradiation of different materials (metals, semiconductors, and dielectrics) with high laser energy densities result in formation of periodic surface ripples called LIPSS. These ripples are produced as a result of the interference pattern of the incident or refracted light and scattered waves propagating parallel to the film surface [32]. These interference patterns give rise to non-uniform heating and result in surface modifications, which remain even after the laser pulse has decayed [33, 34]. The presence of a rough surface is considered essential to produce the scattered waves necessary to see this interference-related feature. Though, LIPSS is an easy way to create nanostructures the quality of patterns over large macroscopic dimensions generally tends to be poor, and as a result, its promise in fabricating useful nanomaterials has been severely limited [35].

1.1.2.5 Pulsed Laser dewetting

Pulsed laser heating has been investigated because of its potential to synthesize nanostructure on surfaces in a robust manner. The important result in SO of metallic films using pulsed laser is that, the morphology progression from an initially smooth liquid film to the final nanoparticle state occurs with intermediate stage that have well defined length scales and complex morphologies. The final nanoparticle stage is characterized by well defined characteristic length scales (Λ) and diameters (D) which vary with initial film thickness as $\Lambda \propto h^2$ and $D \propto h^{\frac{3}{2}}$ [36]. Also under nanosecond pulsed laser irradiation condition, the heating and cooling rate of the metal film is of the order of 10^{10} K/s with a total heating plus cooling time per pulse of ~ 100 ns, which is typically much smaller than the spacing between pulses [37]. This makes possible to capture various complex intermediate morphologies in the evolution process with varying number of laser pulses as shown in Fig. 1.5. However, as we discuss next, it is not possible to have independent control over particle size and spacing.

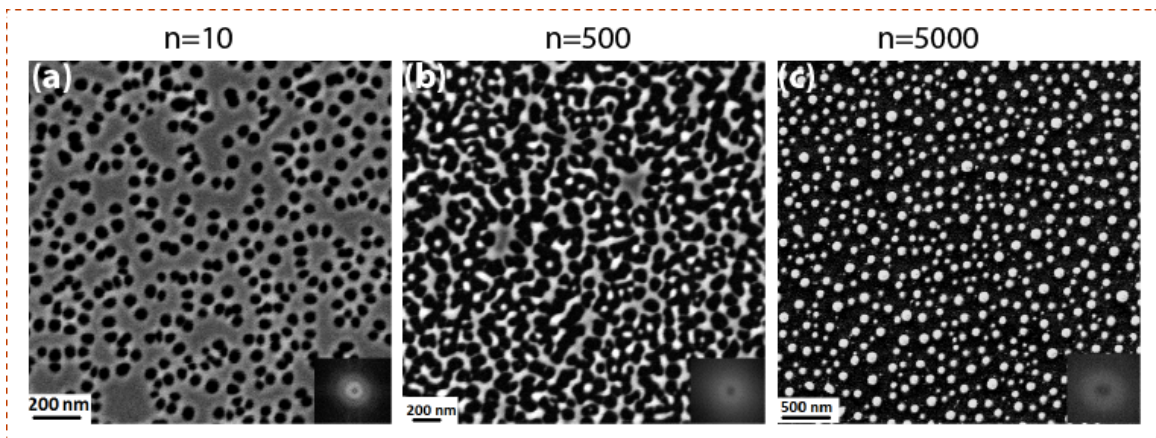


Figure 1.5: SEM images depicting the morphology evolution of a dewetting of Co film under ns pulsed laser irradiation.

1.2 Synthesis of nanostructures by pulsed laser induced spinodal dewetting

1.2.1 Overview

Efficient, economical manufacturing strategies for producing metallic nanostructures & nanocomposites are critical because they can be used in a wide range of applications as mentioned earlier. The plasmonic behavior of metals is central to biological and chemical sensing based on techniques such as localized surface plasmon resonance and surface enhanced raman scattering [2, 3, 38]. Such techniques are expected to spur growth within the biosensing industry, which is forecast to increase by 12% or more to reach revenues of \$16 billion by 2016 [39]. Beyond plasmonics applications, metal nanostructures are important in catalysis for nanowire and nanofiber growth, making and enhancing spintronic materials, improving light emitting characteristics of polymer semiconductors, and use as magnetic materials.

Useful metal nanostructures are typically fabricated either by chemical processes based on self-assembly or by lithography-based nanomanufacturing. Another relatively simple method of forming nanostructures on a surface is based on the dewetting of thin films on an inert substrate. This process, which involves an initial configuration of a smooth film of precise thickness, yields complex patterns, but ones with remarkably well-defined morphology and length scales. When the film is very thin below a thickness of approximately 20 nm, the free energy of the system is primarily due to surface and interfacial forces, and intermolecular forces (such as van der Waals forces), acting across various interfaces. For metal-on-glass systems, the resulting thermodynamic free energy versus film thickness has characteristics of a spinodal phase segregating system, i.e. the curvature of free energy is negative [40, 41]. This feature supports self-assembly of the film by spontaneous dewetting, often referred to as spinodal dewetting, resulting in well-defined nanoscale structures.

Such dewetting is a promising approach to manufacturing nanostructures, as dewetting phenomenon can be applied to the metal film's solid or liquid forms. In solid state dewetting by thermal heating [27, 26, 28], mass transport is primarily determined by surface and bulk diffusion processes and generally exhibits much slower time scales compared to transport in the liquid phase. However, for liquid dewetting, the high melting temperatures of most metals are not easily achieved by conventional heating and require energetic sources, such as ion irradiation, electron irradiation, or laser melting. Pulsed laser melting, especially using nanosecond laser pulses, has helped clarify several fundamental ideas of metal dewetting and also helped establish dewetting as a useful manufacturing route for magnetic and plasmonic metal nanostructures [40, 42].

Here, we discuss the pulsed laser induced dewetting self assembly of single layer metal films on inert substrates. Dewetting occurs due to the amplification of any small perturbations on the thin film's surface under the attractive force due to substrate surface. The attractive force experienced by the films surface is characterized by the disjoining pressure $\Pi(h)$. The variation of the $\Pi(h)$ for ultrathin films ($h < 100\text{nm}$) is such that the thinner parts of the film are at higher pressure than the thicker parts, then any fluctuation of

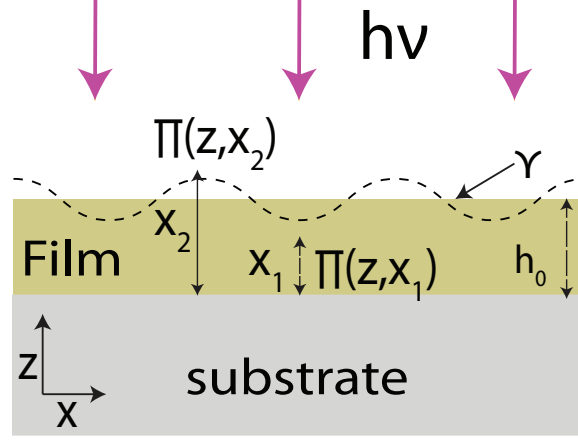


Figure 1.6: Schematic illustrating pulsed laser induced dewetting self assembly of ultra thin films.

the film's surface will amplify the flow of liquid from thinner to thicker parts, while the surface tension tries to oppose this. The fluctuations will amplify whenever there is a decrease in the free energy of the system and triggers a series of morphological changes from Film→Intermediate morphology→ droplet stage. The process of dewetting can be understood by solving the mass transport dynamics using the thin-film hydrodynamic equation in the lubrication approximation of the Navier-Stokes equations [43]. The total Pressure $P(x, z)$ acting on the film at position x was expressed as the superposition of a disjoining pressure (Π) and Laplace pressure due to surface tension as:

$$P(x, z) = \gamma \frac{\partial^2 h(x)}{\partial x^2} + \{\Pi(z) - \Pi(h(x))\}$$

We solved for the evolution of the instantaneous film height h in 1-dimensions (1D) by the mass conservation equation of the form

$$\frac{\partial h(x)}{\partial t} = -\frac{h^3}{3\mu} \frac{\partial}{\partial x} \frac{\partial}{\partial x} \left\{ \gamma \frac{\partial^2 h(x)}{\partial x^2} + \frac{d\Pi}{dh} \cdot h(x) \right\}$$

Where γ is the surface tension of the film-vacuum interface as shown in Fig. 1.6, η is the viscosity of the film, and the disjoining pressure Π for a thin film on substrate is given by $(\frac{A}{6\pi h_o^3})$, where A is the Hamaker coefficient.

Now since z is the coordinate measuring the height $h(x)$, respectively, yielding an evolution equation of the form:

$$\frac{\partial h(x)}{\partial t} = -\frac{h^3}{3\mu} \frac{\partial}{\partial x} \frac{\partial}{\partial x} \left\{ \gamma \frac{\partial^2 h(x)}{\partial x^2} + \frac{d\Pi}{dh} \cdot h(x) \right\}$$

The above equation was solved using linear stability analysis under boundary conditions of no slip at the film/substrate surface $v_z = 0$ at $z = 0$, and no shear stress ($\frac{\partial v_z(z=h)}{\partial x} = 0$) at the film/gas interface with sinusoidal perturbations of form $h(x) = h_o + \epsilon \sin(kx) \cos(\omega t)$. This yielded a dispersion relation for deformation rate ω to wavevector k as:

$$\omega = \frac{h^3}{3\eta} [-\gamma k^4 - \Pi_h k^2] \quad (1.2)$$

Where $\Pi_h = -\frac{A}{2\pi h^4}$, with the negative value signifying an attractive term. From this, the characteristic wavelength $\lambda_{sp} = 2\pi/k_m$ was obtained from the maximum growth rate of perturbations k_m (i.e. $k_m^2 = \frac{-\Pi_h}{2\gamma}$, when $\frac{d\omega}{dk} = 0$) as:

$$\lambda_{sp} = \sqrt{\frac{16\pi^3\gamma}{A}} h^2 \quad (1.3)$$

Also, the time scale of spinodal dewetting $\tau_{sp} = \frac{2\pi}{\omega_m}$ associated with the growth of perturbations with wavelength λ can be evaluated by letting $k = k_m$ in equation 1.2 as:

$$\tau_{sp} = \frac{96\pi^3\gamma\eta h^5}{A^2}$$

This scaling relationship has been studied for ultrathin metal films. This relation provides an important clue to calculate the strength of dispersion forces (A) from experimentally observed fitting parameters. In Chapter 2, we studied the thickness & laser energy dependent spinodal dewetting behavior of Au films through experiments and computations.

1.2.2 Limitations

1.2.2.1 Length Scales

Despite the technological promise stemming from the simplicity of single layer spinodal dewetting in air, one of its major limitations is that the length scales are controlled by the surface tension (γ), strength of Hamaker forces (A), and film thickness (h) as $\lambda = \sqrt{\frac{16\pi^3\gamma}{A}} h^2$. In particular, the only experimentally controllable parameter for a given combination of film and substrate is the thickness of the film h , and hence the approach is limited in its ability to tune the spacing of the resulting nanostructures. For instance, the smallest spacing between particles that can be achieved assuming a continuous film of 4 nm is determined by A and γ . For a typical value of A of $\sim 10^{-18}$ J and γ of 1 J/m², the smallest possible particle spacing is 356 nm ..

1.2.2.2 Diameters

Due to volume conservation, for a given spacing, the diameter of the particle is fixed in spinodal dewetting. The analytical relationship between the diameter (D) of the nanoparticles obtained in spinodal dewetting induced self-organization of thin film of thickness h can be derived basing on the volume conservation as $D = c(\theta)(\lambda^2 h)^{\frac{1}{3}}$. It shows that the size of the nanoparticles depend only on the initial film thickness and length scales and thus, tuning the diameter independently is not possible.

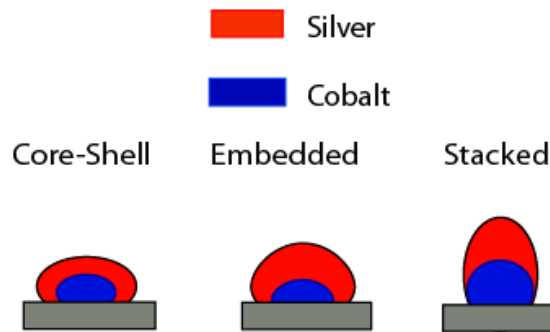


Figure 1.7: Nanoparticles with different morphologies.

1.2.2.3 Long range ordering

Laser induced self organization of thin films results in short range ordering of the nanoparticles. This short range ordering is indicative of dewetting of thin films with a characteristic length scale. Though this simple technique aides in assembly of nanoparticles, this technique is not useful for ordering nanoparticles with periodicity in one or higher spatial dimensions. In laser induced self organization techniques, multiple beam interference irradiation of thin metal films can produce 1D or 2D ordering of metallic nano particles due to thermal gradient effects. But the driving forces from the laser interference process become much weaker in materials with large thermal conductivity, such as materials like Ag and Au.

1.2.2.4 Formation of nanoparticles with different morphologies

Nanoparticles made from multiple components and having different morphologies, for example core-shell, stacked or embedded as shown in Fig. 1.7 , have attracted increasing research interest due to their unique structural features that allow the possibility of combining distinctive properties of varied materials [44, 45, 46, 47]. There are examples showing that these nanomaterials exhibit improved physical chemical properties like magnetism and plasmonics relative to their single-component counterparts [44, 45, 46, 47] . So far only core-shell nanostructures have been successfully fabricated using laser ablation and chemistry based techniques in liquids. In this dissertation, we investigated a novel way to potentially overcome this limitation and to manufacture nanoparticles with different morphologies directly on surfaces by using dewetting of bilayer metal films.

In next sections we show the proposed research plan and we show possible ways to overcome some of these limitations.

1.3 Outline of dissertation

1.3.1 PART I

1.3.1.1 Chapter 2: Pulsed laser dewetting of Au films: Experiments and modeling of nanoscale behavior

Self-assembling and self-organizing techniques are now well-established routes to manufacture nanoscale materials in one or more dimensions. In the context of making metallic nanostructures, the spontaneous dewetting of thin films under thermal treatment has been widely investigated [48, 49, 28, 50, 51, 52]. Amongst the possible heating sources, nanosecond (ns) laser pulses have proved to be important because of their ability to rapidly raise the metal temperature to beyond its melting point and also being able to capture intermediate stages of dewetting due to high quenching rates ($\sim 10^{10}$ K/s for ns pulses). As a result, several important fundamental principles of dewetting, first seen in polymeric systems [53, 54, 55, 56], have been observed and confirmed in metallic systems. For example, in single layer metal films of nm thickness, dewetting of metal films via the classical spinodal instability has been quantitatively verified by a number of investigations. In spinodal dewetting, an initially smooth film is destabilized because attractive intermolecular forces, such as the Hamaker forces, overcome the stabilizing effect of surface tension [57]. In such systems, the ambient/film/substrate free energy behavior is reminiscent of that in immiscible binary systems with spinodal behavior, i.e. the free energy curvature has negative values over a range of concentration, and in this region, the microstructure can spontaneously evolve into segregated regions with well defined length scales. There is ample evidence for metal films that over a thickness range in which the free energy curvature is negative, the dewetting proceeds spontaneously with a characteristic length scale, and analogous to spinodal phase segregation, this behavior is now referred to as spinodal dewetting. In classical spinodal dewetting theory, the length scale λ , as defined by the size or spacing between morphological features, is predicted to scale with film thickness h as $\lambda \propto h^2$, and this has been verified for a number of metal films [58, 41, 48, 37].

The earliest detailed study of pulsed laser dewetting of Au films was reported by Bischof et al [59] on films of ≥ 25 nm. Since then there have been several experimental and theoretical investigations of pulsed laser dewetting in other metals system that included films of a few nm thickness [36, 60, 52]. Those studies have revealed new and useful features of dewetting, such as a distinct difference in the early stage morphology for thin vs thick films, the deviation from spinodal dewetting behavior due to novel nanoscale thermocapillary effects under the laser melting, and the non-equilibrium materials behaviors that can result due to the rapid heating and cooling under the laser pulses [41, 61, 37, 62]. In addition, sophisticated modeling and computational tools, that incorporate the complex mass transport under the highly transient nature of heating have also evolved and now are capable of capturing the dewetting process in a fully three dimensional (3D) manner [63, 51, 64, 65]. In this study, we revisit the behavior of Au dewetting in the thickness regime ≤ 25 nm and specifically between 3 to 16 nm, to establish whether the classical spinodal dewetting behavior for Au is manifested in this region of thickness as well as whether the transition in dewetting mor-

phology is present. We also evaluated the strength of thermocapillary effects in Au dewetting under the ns pulses by theoretical modeling and found them to be much weaker than the dispersion forces, as confirmed in the experiment. Comparison of Au with other metals, including Ag and Co, showed that much smaller dewetting nanostructures occur in Au likely due to its much larger effective Hamaker coefficient. Computations of nonlinear dynamics were utilized to study the morphology evolution in the course of dewetting in 3-dimensions (3D) for a 5 nm thick Au film. This study showed that bicontinuous structures occur during early stages of dewetting, and these break up to form nanoparticles, consistent with experiments.

This study of Au dewetting has implications to nanomanufacturing of Au nanostructures in reliable but robust ways for use in a variety of applications. Specifically, controlling size and spacing of Au nanoparticles on a substrate has implications for catalysis of nanowire growth [66, 67], and in chemical sensing by plasmonic optical effects [68, 69, 2, 3, 38, 70], including by Surface Enhanced Raman Scattering (SERS) [1, 71, 3] and Surface Plasmon Resonance (SPR) techniques [72, 73]. In addition, such investigations providing correlations between experiments and computer models that attempt to capture the complex physics of mass and energy transport under highly transient conditions can lay the foundations for future computer-driven nanomanufacturing scenarios.

1.3.1.2 Chapter 3: Nanomaterials synthesis by a novel phenomenon: The nanoscale Rayleigh-Taylor instability

There are many applications of nanostructures, such as nanoparticles (NPs), of any variety of hard matter, including metals, ceramics and semiconductors, that require their arrangement on surfaces with precise control over size and spacing. Some broad categories of applications include solar energy harvesting, biosensing, and photocatalysis [74, 75, 76, 77, 78, 79, 80, 81, 82]. In recent years the spontaneous deformation of a thin film leading to nanoscale patterns governed by self-organizing principles have generated great interest. The reason is that by controlling the choice of materials, such as film and substrate, intrinsic forces of surface tension and dispersion can be changed to modify the time and length scales of pattern formation [83, 59, 37]. However, while the reliance of intrinsic forces leads to robustness and predictability in pattern formation, such thin film self-organization invariably limits the control over pattern length scale to the form $\lambda \propto h^n$, where λ is the self-organized length, h is the film thickness and n varies depending on the conditions used. For instance, in the well studied *liquid-phase* spinodal dewetting instability, the pattern length scale λ varies with film thickness h as $\lambda \propto h^2$ [56, 55, 83, 36] and could be modified somewhat by introducing thermal gradients [49], or by relying on solid state mass transport [84]. While some ways to overcome this constraint has been demonstrated for polymer liquid films, such as by chemical or morphological modifications to the substrate surface [85, 86, 87], similar flexibility has not been shown for the vast majority of high temperature fluids, such as metals and semiconductors.

Here we propose a novel way to decouple the self-organized length scale from film thickness by using the Rayleigh-Taylor (RT) instability. From a historical perspective, the length scale in the *classical* RT instability pattern forming instability, such as the beading up of a water film on the ceiling, does not depend on the thickness of the film [88]. But, the *classical* RT instability cannot be observed in nanoscale thin films

because the acceleration forces acting on the fluid come from gravity, thus requiring thick films (thickness greater than the capillary length of order 0.1 mm). On a fundamental level, the primary requirement for the RT instability is that a less dense fluid should be accelerated into a more dense fluid [89, 90]. This interface destabilization between two fluids can be achieved in a number of different ways [88], as evident by the large number of examples from an extremely diverse range of systems, including in astronomical structures such as black holes and supernova [91, 92, 93], geophysical phenomenon [94, 95], fusion [96, 97, 98, 99], and bulk fluid-fluid interfaces [100, 101, 102].

The new idea proposed in this work is based on the interesting thermal behavior found when a film-fluid interface is heated rapidly by short laser pulses, with the fluid being converted into gas. Since the temperature falls rapidly on going away from the film/gas interface, strong gas pressure gradients are generated. This leads to a local, film-thickness dependent, pressure that can overcome the stabilizing effects of surface tension and also dominate the destabilizing effects of intermolecular attractions found in nanoscale thickness films. When this result is incorporated into mass transport models, linear analysis predicts a classical RT instability scaling behavior. We performed experiments involving nanosecond (ns) pulsed laser melting of nanometer thick Au films immersed in glycerol liquid. The ensuing nanoparticle size and spacing was studied as a function of laser energy and film thickness. The results were in excellent agreement with the theoretical predictions of the RT instability, including the independence of nanoparticle spacing on film thickness. To the best of our knowledge this is the first observation of RT instability at the nanoscale and its application towards synthesizing materials in a controllable manner.

1.3.1.3 Chapter 4: DC electric field induced phase array self-assembly of nanoparticles

Spatially periodic metal nanoparticle arrays are important in a wide range of applications, such as for plasmonic waveguiding [103], for nanoscale lensing [104, 105], for catalysing the growth of ordered carbon nanotubes [106] and as Raman active substrates [107]. However, one of the challenges is to fabricate large area periodic arrays of nanostructures in a reliable and cost effective way, and this has led to intense research in nanoscale fabrication methods. Several fabrication techniques based on lithography and bottom up self assembly routes have emerged to synthesize nanoparticles in arbitrary geometries, size, and one- or 2-dimensional (1D or 2D) spatial arrangement. Lithography techniques utilizing ultraviolet (UV), e-beam or ion beam energies are all powerful ways, but are ultimately limited by their high cost, complicated mask technology, development of appropriate resist materials and most importantly, requirement of sophisticated instrumentation. Laser-induced forward transfer (LIFT) [108, 109] and a combination of focused ion beam (FIB) and thermal annealing [110] have also been used to synthesize 1D particle arrays. The major limitations of LIFT are the difficulty in controlling the inter particle spacing in sub-micron scale and achieving large area of nanoparticle arrays, since particles are produced in a serial manner. Thermal annealing is complicated because of metal-substrate chemical interactions and metal diffusion into the substrate, which may cause impure particle arrays. Self assembly methods like nanosphere lithography (NSL) [111] and pulsed laser induced self-organization [112, 113, 114] are easy and cost effective ways to fabricate nanostructures, but they also have their own limitations. Nanosphere lithography uses self-assembled monolayers

of polystyrene spheres as evaporation masks, and presently, only a hexagonal geometry of nanoparticle patterns can be obtained. In laser induced self organization techniques, multiple beam interference irradiation of thin metal films [115, 116] can produce 1D or 2D ordering of metallic nano particles due to thermal gradient effects. But the driving forces from the laser interference process become much weaker in materials with large thermal conductivity, such as materials like Ag and Au.

Within the context of laser interference processes, the phenomenon of LIPSS (laser induced periodic surface structure) has been widely investigated, both from a fundamental perspective as well as a way to make ordered nanostructures [117, 118, 119]. In LIPSS, a spontaneous spatially periodic pattern emerges simply under irradiation by a single coherent laser beam. The pattern is a result of an interference phenomenon between the incident light and scattered light [120, 121, 122, 123, 124]. For this reason, LIPSS is a highly attractive phenomenon for fabrication of templates and/or nanostructures because of its extremely simple experimental implementation [125, 126]. However the patterns produced by LIPSS are often low quality with defects like bifurcation and domain misorientation (ripples), resulting in poor ordering over large areas. In fact, the inability to eliminate defects in LIPSS patterns has limited its implementation in practical technologies.

In this work, we show a scientifically interesting and practical new way to significantly enhance the quality of the spontaneous 1D ordering arising under the irradiation of a surface by a single laser beam. When an initially near-random arrangement of metal nanoparticles on glass (SiO_2/Si) substrates was irradiated by laser light a traditional defective LIPSS pattern resulted. However, when a DC electric field was applied to the underlying glass substrate, significant changes to the 1D ordering quality and coverage area were observed. Single-crystal like patterns over macroscopically large areas could be achieved under specific field orientation and magnitudes.

1.3.2 PART II

1.3.2.1 Chapter 5: Morphology transitions in bilayer spinodal dewetting systems

The study of the behavior of self-organizing processes, which appear in systems ranging from geographical to nanoscale sizes, is of fundamental interest because it sheds light on the relationship between the various intrinsic forces and the resulting unique ordered shapes, structures, and morphologies. A well known example of this is the behavior of diblock copolymer thin films [127, 128]. In these systems, thermodynamic immiscibility between the two blocks lead to self-organized structures with lamellar, cubic or other arrangements, such that the contact between similar and dissimilar components are maximized and minimized, respectively. Since the resulting attributes of size, shape and arrangement define the various functionalities of the material, the study of such behavior is of considerable practical significance. One naturally occurring process that is broadly applicable to polymer and non-polymer systems, like metals, is self-organization by dewetting [57, 129, 55, 130, 48, 37]. In dewetting a liquid or solid film in contact with a surface spontaneously breaks-up due to internal forces to form features with well defined size and shape. However, unlike

the case of diblock copolymers, where energy minimization leads to good understanding of the patterns, the behavior of dewetting systems requires a dynamical approach [131, 132, 53].

Over the past 50 years, spontaneous dewetting has been studied quite extensively, especially in single-layer films on a substrate. Current understanding divides dewetting into two categories. One is spinodal dewetting, which leads to structures with spatially ordered features, and hence is of substantial interest [131, 55, 130, 48, 37]. The other is nucleation and growth, in which the film overcomes an energetic barrier in its pathway to the deformed state, which may or may not consist of ordered features [129, 133]. An important characteristic of spinodal dewetting systems is that the free energy of the film, as a result of the attractive and repulsive surface and intermolecular forces, shows the negative curvature reminiscent of spinodal phase segregating systems [57, 56]. Spinodal dewetting proceeds by an early stage perturbation of the initially flat film that selects a preferred length scale, and one which can be well explained by simple linear theories [57]. However, the subsequent evolution or ripening of the film shape, leading to rupture and exposure of the substrate, which is of substantial practical relevance since it controls the visible intermediate stage morphologies, is determined by a complex and highly non-linear evolution of the film height [132]. Nevertheless, a simplifying theme has been observed in various studies of single-layer film dewetting, in that the early-stage ripening morphology can be quite accurately predicted by the curvature in the film-thickness dependent free energy $\Delta G(h)$. As first identified by Sharma and Khanna [53], the position of the minima in the free energy curvature identifies a morphological transition from a bicontinuous stage (to the left of the minima) to a hole-like stage (to the right of the minima). The underlying physical reasoning for this behavior is attributed to the role of the free energy curvature in the dynamical equations that determine the transport of matter, much like the case of spinodal phase segregating systems [134]. While the general validity of this observation has been verified in single-layer polymer [54, 135] and metal films [41, 136], its applicability to describing the behavior of more complex bi-layer films or higher order spinodal dewetting systems, has not been evaluated thus far.

In this work, we have investigated the morphological phase diagram for spinodal dewetting in bi-layer systems, which comprise of two liquid layers (bi-layers) on a substrate. As compared to single-layer films, the complexity of the free energy and dynamics in bi-layer systems is significantly higher [137, 138, 139, 140] than the single-layer because of the increase in the pairs of interfaces (three in bi-layers vs one in single-layer) and the possibility for deformation to occur via bending and squeezing modes, which are absent in single-layer films. As a prototypical system, we have studied bi-layers of metallic liquid films of Co and Ag on a low energy SiO_2 surface. Because of the minimal chemical interactions between the various components, this system provides a good way to explore spinodal dewetting in non-interacting systems, as previously confirmed from the behavior of patterning lengths [42]. In addition, the nanoparticle structures of the final stable state predicted by the non-linear modeling of this system [63] suggest potential applications in energy harvesting and sensing as bimetallic materials [141, 142, 143, 144, 145]. Nanosecond pulsed laser dewetting experiments were performed to generate the early-stage ripening morphology as a function of the thickness and arrangement of the two liquid layers. From this we could construct the phase diagram and determined that only two distinct morphologies are evident - bicontinuous (BC) structures and holes (H) - similar to the single-layer case. We also determined that the bi-layer system can show single or multiple

transitions between these morphologies with changing film thickness. The bi-layer free energy curvature accurately predicted the location of the first morphology transition, much like the single-layer case, but did not predict the second. However, interestingly, the entire bi-layer morphology and both transitions can be accurately predicted by the behavior of the two single-layer films, and in this regards, the curvature argument is still a valid one. The implication of this finding is that despite the vastly more complex length scaling and non-linear evolution behavior of the bi-layer systems, its ripening morphology follows a simple underlying principle.

1.3.2.2 Chapter 6: Formation of organized nanostructures from unstable bilayers of thin metallic liquids

Nanostructured surfaces and nanomaterials, such as nanoparticles that show multiple useful physical characteristics (for instance, magnetism and plasmonics), could be very useful towards sensing and detection, including of surface chemical interactions. As a result, advances will be to applications in biocatalysis [146, 147, 148], biosensing [149], high-density magneto-optical technologies [150], and semiconductor computing and switching utilizing spintronic effects [151]. Such a surface can be envisioned to be made from nanostructures of different metals, such as of Ag (which is plasmon active) and Co (which is ferromagnetic), in which the morphology characteristics (for instance, core-shell or composite structures), will determine the physical response [44, 152]. Therefore, control of the nanoscale features, especially at length scales below the diffraction limit of light, is an ongoing challenge.

There are limited techniques, such as lithography [45], solution processing [46], and self-organization [42], that have demonstrated the synthesis of such multi-component nanomaterials. Spontaneous self-organizing processes that lead to nanostructure formation are often attractive because of the intrinsic robustness and low cost. One such process that is being harnessed to create complex nanostructures is the spontaneous spinodal dewetting of thin polymeric liquid films from its contact surface [56, 55, 53]. For an ultrathin film on a non-wetting substrate, long-range intermolecular attractive dispersion forces between the film and substrate, with magnitude determined by the Hamaker coefficient A , lead to an unstable thermodynamic free energy which can have a spinodal character, i.e. the free energy curvature < 0 . Consequently, for such thin films, a height perturbation of the liquid film surface, such as by capillary waves, can result in a free energy decrease, leading to spontaneous spinodal dewetting [56, 55]. In order to observe this behavior in metals, which have extremely high melting temperatures, practical ways to access the liquid phase are necessary. Therefore, studies of pattern formation in metal films have focused on the use of ion irradiation [153, 154] or pulsed laser irradiation [155, 59, 37].

Laser-irradiation of metallic films exhibit a variety of spatio-temporal instabilities leading to formation of different nanomorphologies [156, 42, 49, 52]. The present paper is motivated by the recent experiments on dewetting of non-reactive, immiscible metallic bilayers done in our group [42], and the need to better understand the physical mechanisms leading to spatial ordering of particles and the morphological pathways towards the final particle morphologies. The experimental [157, 158, 159, 160, 161, 162, 163, 164] and theoretical [165, 166, 167, 168, 169, 170, 138, 171, 172, 173] studies of the instabilities and dynamics of bilayer

thin films so far have been largely limited to aqueous and polymer systems under isothermal conditions. Non-isothermal dewetting even in such more conventional systems has not been fully investigated theoretically. Indeed, in Refs. [165, 166] the equation set that accounts for the Marangoni effect is derived, but only the analysis and some computations in the isothermal case are performed; and in Refs. [171, 172, 173] either a special set of Hamaker coefficients is considered, such that dewetting exhibits autophobic behavior, or in addition a longitudinal temperature gradient is considered.

Pulsed laser irradiation of single-layer thin films has been shown to introduce thermocapillary effects along the film - ambient surface and thus influence pattern formation [174, 175, 49]. The underlying reason for the appearance of the thermocapillary effect is a thickness-dependent temperature due to the dependence of laser light reflectivity and absorption on the local thickness [49]. In this work, for the first time we show that similar thermocapillary effects appear in bilayer films irradiated by the laser. As a consequence, it is necessary to study the non-isothermal dewetting instability in order to better predict future experimental investigations of the morphology evolution. Therefore, in this work we explore theoretically and computationally the isothermal as well as non-isothermal instabilities and morphological evolution in laser-melted bilayers. The major sections of the paper are divided as follows. In Sec. II we detail the bilayer evolution equation and the thermal problem. The systems under consideration are metallic bilayers (of Ag/Co and Co/Ag) in contact with a transparent SiO_2 substrate formed on a reflective Si support layer. We evaluated the steady state bilayer film temperature profile by utilizing the mean substrate temperature estimated from an elaborate thermal model of transient heating and melting/freezing. In Sec III, Linear stability analysis was performed to obtain the dewetting instability length scales for the isothermal as well as non-isothermal cases. These results were compared to experimental measurements of length scales for the Ag/Co and Co/Ag bilayers presented in [42]. In our recent work, we found using an energy rate analysis approach that the experimental results were well predicted if they were bounded by two sets of Hamaker coefficients. This was a consequence of the different techniques used to calculate the Hamaker values. Here we followed a similar approach in the linear analysis. We found that the non-isothermal results were a better bound to the experimental results as compared to the isothermal case. Consequently, this motivated us to pursue the full non-linear evolution dynamics in the non-isothermal as well as isothermal cases. This work is presented in Sec. IV. The calculations were performed for the Ag/Co and CO/Ag systems as a function of the upper layer thickness. We found differences in the morphological characteristics, including core-shell, embedded, or stacked nanostructure morphologies. In addition, we also found that for certain cases, the non-isothermal evolution predicts different morphologies from the isothermal case. These results are likely to be very useful towards guiding future experiments that investigate the correlation between morphology and physical characteristics.

1.3.3 Summary and future work

1.3.3.1 Chapter 7: Summary and future work

A summary of the main results of the dissertation as well as potential future directions of research pertaining to liquid based patterning of metal films is briefly discussed. While this thesis was focused on investigating nanoparticle formation from thin continuous films, we have seen preliminary indications that irregular nanostructures can also be changed into nanoparticles in a very controlled manner. Specifically, early results are presented in Ch 7 that show that laser melting of irregular nanostructures inside bulk fluids leads to predictable behaviors of the length scales and diameters. This potentially opens out a new line of investigation, i.e. self-organization from irregular shaped structures.

Chapter 2

Pulsed laser dewetting of Au Films: Experiments and modeling of nanoscale behavior

(Reported to Journal of Materials Research, vol 28, 1715 (2013))

2.1 Summary

Ultrathin metal film dewetting continues to grow in interest as a simple means to make nanostructures with well-defined properties. Here we explored the quantitative thickness-dependent dewetting behavior of Au films under nanosecond (ns) pulsed laser melting on glass substrates. The trend in particle spacing and diameter in the thickness range of 3 to 16 nm was consistent with predictions of classical spinodal dewetting theory. The early stage dewetting morphology of Au morphology changed from bicontinuous-type to hole-like at a thickness between 8.5 to 10 nm, and computational modeling of nonlinear dewetting dynamics also captured the bicontinuous morphology and its evolution quite well. The thermal gradient forces were found to be significantly weaker than dispersive forces in Au due to its large effective Hamaker coefficient. This also resulted in Au dewetting length scales being significantly smaller than those of other metals such as Ag and Co.

2.2 Methods and techniques

Au films with thickness from ~ 3 to 16 nm were deposited in high vacuum ($\sim 1 \times 10^{-8}$ Torr) by electron beam deposition at room temperature onto commercially obtained, optical quality, SiO_2/Si wafers consisting of 400 nm thick thermally grown oxide layer on polished $\text{Si}(100)$ wafers [36]. The wafers were cleaned in methanol, acetone, and DI water. The deposition rate used here was typically ~ 1.5 nm/min as confirmed by atomic force microscope (AFM) step height measurements. Energy dispersive X-ray spectrometry (EDS) was used to measure the Au counts of the deposited films in a scanning electron microscope (SEM). The EDS counts were converted into an equivalent thickness value by using calibration based on step-height measurements of the film thickness. Surface roughness of the deposited films were measured by AFM and established an upper limit of 0.5 ± 0.2 nm for the average root mean square (RMS) roughness over the entire thickness range. Deposited films were irradiated by a varying number of pulses n ($\sim 10 - 10500$) from a 266 nm ultraviolet laser having a pulse width τ_p of 9 ns. Irradiation was performed at normal incidence by an unfocused laser beam of area 1×1 mm² at a repetition rate of 50 Hz. The dewetting morphology was investigated as a function of film thickness h , and the number of pulses n , which typically ranged between 10 to 10,500 pulses, for irradiation at laser energies at or just above the melt threshold of the films. For each thickness the melt threshold was determined by a visible roughening of the metal film surface, as detected under high-resolution SEM within the longest time scale of the experiment (i.e. after 10,500 laser pulses) [37, 41]. The range of E used for the thickness regime investigated here was $40 \leq E \leq 100$ mJ/cm². For this irradiation condition, the heating and cooling rate of the metal film was of the order of 10^{10} K/s with a total heating and cooling time per pulse of ~ 100 ns, which was much smaller than the spacing between pulses, which is 20 ms. Consequently, it has been quantitatively shown earlier by Favazza et al. [62] that negligible contribution to the morphology evolution is expected from processes in the solid state. Hence, any morphology change occurring is primarily during the liquid phase following each pulse. It was confirmed by EDS measurements that the laser irradiation did not result in substantial evaporation of the Au, even after the longest irradiation experiments of 10,500 pulses. In order to better understand the transient thermal

behavior and magnitude of thermal gradients in Au films, thermal modeling for Au films was computed using COMSOL [176] using an optical thermal model as mentioned in ref. [176]. This modeling included the use of temperature dependent material parameters and all phase changes.

2.3 Results and Discussion

2.3.1 Spinodal Dewetting in Au films

Figure 2.1(a-c) shows the dewetting morphology observed following irradiation of 12 nm Au films at an energy density $E = 70 \text{ mJ cm}^{-2}$ for increasing number of laser pulses n . After a few pulses, $n = 10$, the dewetting morphology is characterized by holes as show in 2.1(a). As n is increased the metal/substrate contact lines recede to the edge of the holes resulting in a network of coalescing polygon features and continued irradiation results in the formation of nanoparticles primarily at the junctions of the polygons [36]. Quantitative information about the spatial characteristics of these morphologies was obtained by evaluating the fast Fourier transform (FFT) of the SEM image contrast, which is related to the dewetting film's height variations. The resulting FFT information of the contrast correlation is shown in the inset of each figure, and the important information here is the annular form for each of the films. This annular FFT is indicative of a narrow band of characteristic length scales L for the height variations on the surface. This is an important observation given that the dewetting morphology can progress via either of the three pathways: homogeneous nucleation, heterogeneous nucleation, or spinodal dewetting [129]. In the case of homogeneous nucleation, the features are randomly distributed, both spatially, and in time, and no characteristic length scale should appear in this type of dewetting [133]. Heterogeneous nucleation can occur due to defects, impurities or other experimentally imposed heterogeneities. In this type of dewetting, a characteristic length scale could appear at the early stages of dewetting only in the presence of available ordered nucleation sites. However, we have not observed spatially ordered heterogeneities on the substrate surface, as well as on the as-deposited films, prior to irradiation.

The characteristic length scale associated with spinodal dewetting is established at the very early stages of film deformation [48]. The early stage undulations, which occur prior to the appearance of large height variations in the film, are extremely difficult to capture experimentally. However, the subsequent morphology, which is a result of ripening of the initial undulations, forms as dewetting progresses and has length scales directly related to the initial length scale. Therefore, as shown by many authors, the final nanoparticle length scale, can be used as a measure of the thickness-dependent behavior [55, 36]. Here, the length scales were measured at different stages of the dewetting process as a function of film thickness. In Fig. 2.1(a-c), the progression of the morphology is shown for the 12 nm film as a function of laser pulses between 10 and 10,500 shots. Fig. 2.1(d) is the radial distribution function (RDF) for each measured stage of the 12 nm film. From the position of the peaks in such RDF measurements, obtained directly from the FFT's, it was possible to generate the characteristic length scale present in the pattern at each stage. The initial rapid increase in the characteristic length scale corresponds to the increase in the average size of the initial nanomorphologies, either bicontinuous structures or holes, while the decrease corresponds to break-up of

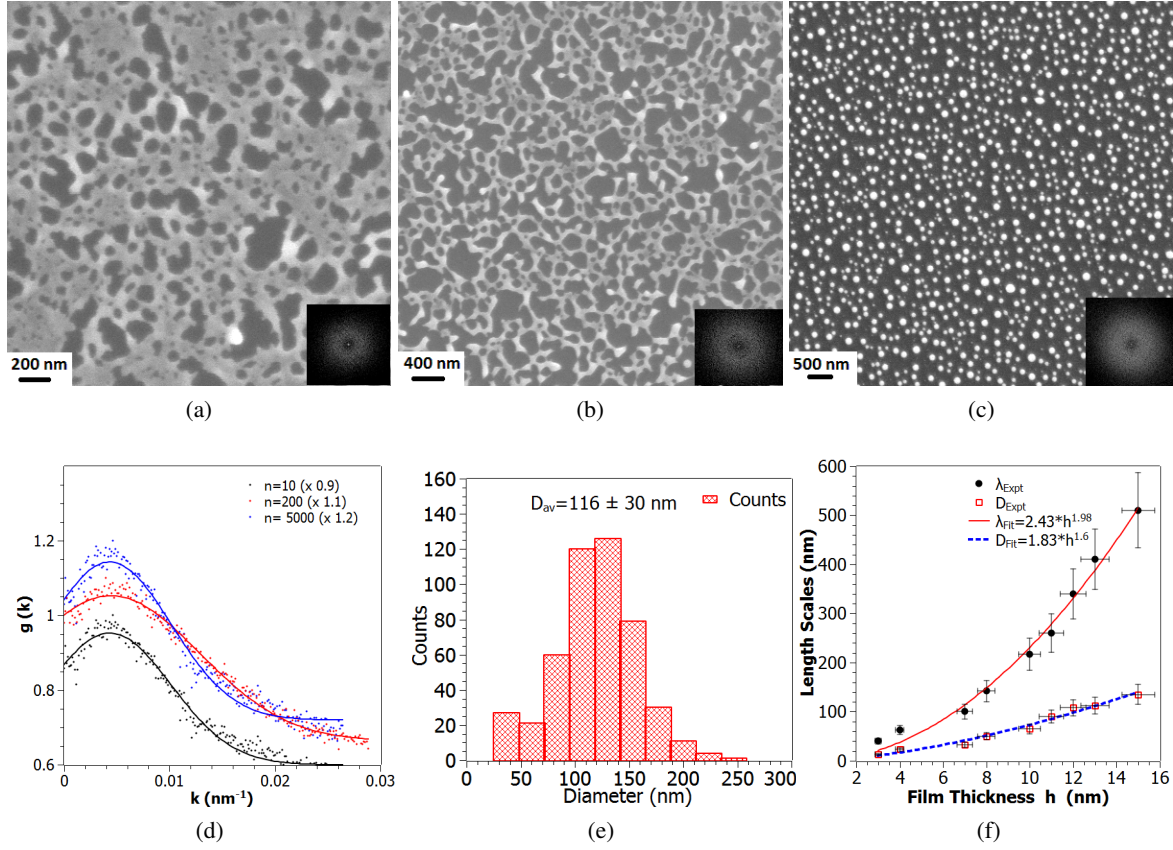


Figure 2.1: (a-c) SEM images of progression of dewetting in 12 nm thick film with increasing number of laser pulses n (10, 200, 10500). (d) Plot of the radial distribution function (RDF) for each stage of dewetting with Gaussian peak fitting. The peak position in the RDF was used to estimate the characteristic length scales. (e) Size distribution and average diameter of nanoparticles from SEM image of Fig. (c). (f) Analysis of the various length scales in the final robust nanoparticle state as a function of film thickness. The fits show the exponent in good agreement predictions from with linear thin film hydrodynamic theory.

these nanomorphologies into nanoparticles, with long time value representing the characteristic length scale of the film. The final size distribution of the nanoparticles was established to be monomodal as shown in Fig. 2.1(e).

To confirm quantitatively if this was indeed classical spinodal dewetting, we investigated the experimental variation of the nearest neighbor inter-particle spacing λ as a function of the film thickness h . From thin film hydrodynamic theory of spinodal dewetting it is known that the λ should vary with film thickness h as $\lambda = \sqrt{\frac{16\pi^3\gamma}{A}}h^2$, where γ is the film-vacuum interface energy and A is the Hamaker coefficient characterizing the strength of the intermolecular dispersion forces [57, 36]. In Fig. 2.1(f - closed symbols) the experimentally determined variation of length scales λ and average particle diameter D is plotted with film thickness. A power law fit to the variation in λ yields $\lambda = 2.43h^{1.98}$, which is in excellent agreement with the theory predicted trend [Fig. 2.1(f - solid line)]. The variation in D of the nanoparticles as a function of film thickness h is shown in 2.1(f - open symbols). A power law fit to our experimental data gives $D=1.6h^{5/3}$, which is in good agreement with the theory prediction based on volume conservation arguments [37, 55]. Hence, these experimental studies in the 3 to 16 nm thickness range confirmed that Au dewets by the classical spinodal dewetting mechanism.

2.3.2 Experimentally Determined Hamaker Coefficient

Surface forces between two bodies in close proximity plays an important role in thin film sciences. Dispersion forces such as the van der Waals force, which arises from the interaction of oscillating dipoles, has a role in controlling many aspects of the behavior of materials. It controls or influences macroscopic phenomena such as surface tension, wetting behavior, and adhesion. The van der Waals interaction can be quantified through the Hamaker constant A , which is a material property [177, 178]. Israelachvili [177] has provided a description of the different methods available to obtain the Hamaker constant for different materials and configurations, including multilayer structures, such as the one involved in thin film dewetting scenarios. In fact, Spinodal dewetting offers a potential route to estimate the effective Hamaker constant A_{eff} . Since

Table 2.1: Effective Hamaker coefficients A_{eff} of various metals estimated from h^2 behavior of experimentally measured dewetting length scales. Theoretical values obtained from ref. [177] are also shown. For Iron, the A value was estimated from length scales vs film thickness data reported in ref. [58]. The experimentally determined transition thickness and range of correlation lengths is also shown.

#	Metal	A_{eff} (J)	A_{Theory} (J)	$h_{T,Exp}$ (nm)	l (nm)
1.	Cobalt	1.41×10^{-18} [37]	13.1×10^{-19}	~ 4	0.4 - 0.5 [37, 40]
2.	Silver	4.78×10^{-18} [41]	1.33×10^{-19}	~ 10	0.9 - 1 [41]
3.	Gold	9.784×10^{-17} (Present Work)	1.76×10^{-19}	~ 9	0.2 - 0.3
4	Copper	1.56×10^{-17} [51]	2.08×10^{-19}	-	-
5.	Iron	2.3×10^{-18} [58]	2.0×10^{-19}	-	-

the characteristic length scale for spinodal dewetting is known to vary as $\lambda = \sqrt{\frac{16\pi^3\gamma}{A}}h^2$, the power law fit to experimentally observed spacing for metal films yields the form $\lambda = Bh^2$ [37], with height expressed in

nanometers, where 'B' is the pre-exponential factor expressed in nm⁻¹. From the experimentally established pre-exponent factor of B , the Hamaker coefficient for metals can be estimated upon using the known value of γ (in J/m²) [179]. Previous works have extracted the effective A values for other metals in similar manner, including for Ag, Co, Cu, and Fe, and these are tabulated in Table 2.1 and compared to the theoretical predictions taken from ref. [177].

2.3.3 Transition Thickness

In spinodal dewetting of thin metal or polymer films the final nanoparticle stage occurs through the morphology sequence Film $\rightarrow$ Intermediate stage $\rightarrow$ Nanoparticles. The intermediate stage morphology can be either of bicontinuous type or hole-like. More interestingly, it has been observed in metal and polymer films [41, 54, 53, 40] that below a specific thickness the observed intermediate stage morphology is bicontinuous while above it, it is hole-like and this thickness value is termed as the transition thickness h_T . Theoretically, h_T for a single layer film is strongly correlated to the minima of the free energy curvature, which, in turn, is the second derivate of the thickness-dependent free energy of the film/substrate system [41, 53, 40]. The free energy G and its curvature for a single layer film on a substrate are given by [41, 40]:

$$\Delta G = \frac{A}{2h^2} - \frac{Ah_c^6}{24h^8} + S^p \exp(-h/l) \quad (2.1)$$

$$\frac{\partial^2 \Delta G}{\partial h^2} = \frac{3A}{h^4} - \frac{3Ah_c^6}{h^{10}} + \frac{S^p}{l^2} \exp(-h/l) \quad (2.2)$$

where A is the Hamaker coefficient of the vacuum/metal - metal/substrate interface, l is the correlation length, S^p is the spreading coefficient, and h_c is defined as $\frac{A}{h_c^2} \frac{3^{4/3}}{8} = -2\gamma \sin^2(\theta/2)$, where γ is the surface energy of film vacuum interface and θ is the equilibrium contact angle of the film on the substrate. From Equations 2.2 and 2.1 in principle one could predict the transition thickness h_T if all the materials parameters are known. However, one of the largest uncertainties exists in the value of the correlation length l , which can vary between 0.1 to 1 nm, and to which h_T is very sensitive. Therefore, experimental measurements of h_T can also aid in better estimating the value of the correlation length l . In the case of our Au measurements, we determined the location of the transition thickness by evaluating the early stage morphology as a function of h , as shown in Fig. 2.2(a-e). From this measurement it was clear that the transition from the bicontinuous morphology to a hole-like state occurred for film thickness between 8.5 and 10 nm. Next, we utilized Eq. 2.1 and 2.2 with the experimentally determined A_{eff} from Table 2.1 and found that the possible range of the correlation length was 0.2 to 0.3 nm in order for the h_T to be in the interval from 8.5 to 10 nm. In Fig. 2.2(f), we have plotted the free energy $G(h)$ and its curvature $G(h)''$ for A_{eff} and a correlation length of 0.2 nm, which yields the transition thickness of 9 nm. The values of other constants used are as shown in Table 2.1 [41].

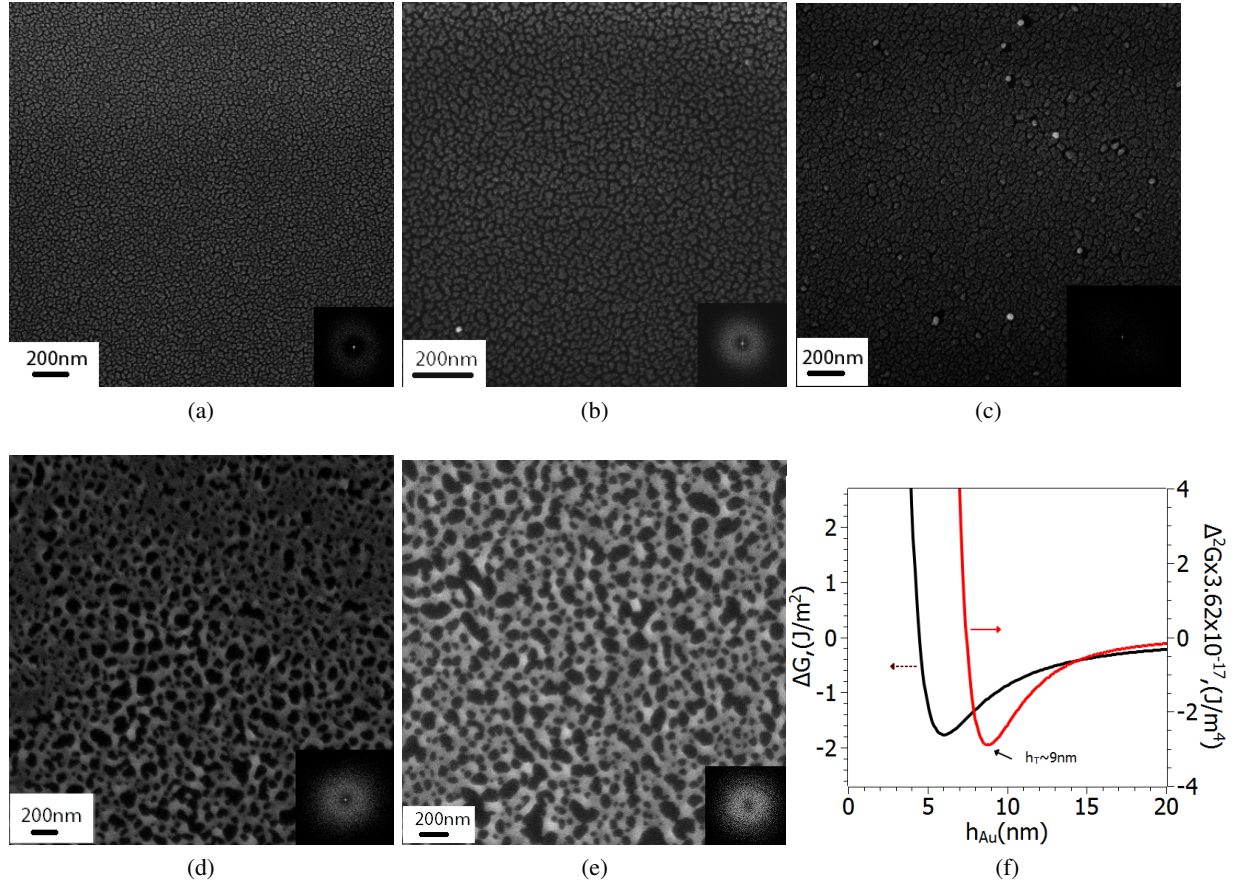


Figure 2.2: (a)–(e) SEM images of the early stage dewetting morphologies following irradiation by 10 laser pulses. The film thickness from (a) to (e), corresponds to 3, 4.5, 8.5, 10, 16 nm, respectively. Also shown in the inset of each figure is the FFT of the contrast correlations of the SEM images. The annular spectrum indicates that a well-defined length scale characterizes each pattern. (f) Plot of the free energy curvature versus film thickness using equations in [41]. The transition thickness h_T corresponds to the minimum in the curvature and occurs at $h_T \sim 9$ nm.

Table 2.2: Materials values of Au used in thermal simulation, with the thermal values for substrate taken from [63, 176].

Quantity	Description	Value [Reference]
$R(h)$	Thickness-dependent reflectivity	Calculated from Ref. [176]
$L\left(\frac{J}{Kg}\right)$	Heat of formation	63700 [180]
$T_m(K)$	Melting temperature	1337.73 [180]
$\rho_{Au,T_m}\left(\frac{Kg}{m^3}\right)$	Film density at melting point	$19501.44 - 0.6933844T - 2.041944E^{-4}T^2 + 4.297982 E^{-8} T^3$ if $T \leq T_m$ [181]; 17360 if $T \geq T_m$ [180]
$k_{Au}\left(\frac{W}{m-K}\right)$	Film thermal conductivity	$(330.6431 - 0.02536626T - 8.191375 E^{-5}T^2 + 6.792908E^{-8}T^3 - 2.15362E^{-11}T^4)$ [182] if $T \leq T_m$ $(40.28092 + 0.06996394T - 1.851678e-5T^2 + 1.711743e-9T^3 - 6.17021e-14T^4)$ if $T \geq T_m$
$C_{p,Au}\left(\frac{J}{Kg-K}\right)$	Film heat capacity	$399352.2T^{-2} + 114.8987 + 0.03228805T$ if $(T \leq T_m)$; 169.3423 if $(T \geq T_m)$ [183]
$\gamma_T\left(\frac{mJ}{m^2K}\right)$	$\frac{d\gamma}{dT}$	0.18

2.3.4 Estimation of thermocapillary effects

The deviation of length scales from classical spinodal behavior due to a novel effect was observed in an earlier study of the pulsed laser dewetting of Co and Fe [49]. The underlying reasons for that was novel nanoscale thickness-dependent heating effects that introduced thermocapillary forces in the dewetting process. A heat transport model that captured this transient thickness-dependent heating of ultrathin films under a laser pulse was further developed by us and is described in detail in [176]. One of the key ingredients of this transient thermal model is to account for the thickness-dependent optical reflectivity in the nanoscale thin films. Thermal model was applied to the Au films studied here in order to estimate the contribution of thermocapillary effects on the dewetting of Au. The quantitative accuracy of the model was verified by calculating the thickness dependence of the melt threshold laser energy, as shown in Fig. 2.3(a - open symbols), which showed excellent agreement with the experimentally determined melt threshold [Fig. 2.3(a - closed symbols)]. An important effect that is evident here is that the energy required to melt the Au film does not change monotonically with increasing thickness. In fact, around a thickness 6 to 8 nm, the required energy passes through a minimum, and eventually reaches a stable value for very thick films. This effect, due to the thickness-dependent reflectivity and transient nature of the heating pulse, is at the heart of the novel thermocapillary effect reported in ref. [49] as well as the unusual processing dependence of nanowire formation reported in ref. [176]. Essentially, since the local film temperature is thickness dependent, one could expect to see a gradient in surface tension for a film with thickness undulations. In dewetting theory, it is recognized that surface undulations initiate the dewetting process, and therefore these undulations, in conjunction with the laser pulse, cause the surface tension gradients and ensuing thermocapillary effects that

modify classical dewetting behavior in metals such as Co and Fe.

For the case of Au and at a fixed value of the laser energy density, the potential magnitudes of the thermal gradients due to undulations in film height were estimated. In Fig. 2.3(b) the modeled temperature vs time profiles are shown for two different thickness and a fixed value of laser energy density. From this it is clear that at any given time, the two thicknesses result in different temperatures, and hence, the film height undulations will have different instantaneous temperatures. The magnitude of the thermal gradient ($T_h = \frac{dT}{dh}$) as a function of varying film height at the instant of melting was estimated using the thermal model, and this is shown in Fig. 2.3(c - dashed line). The order of magnitude of the effect in Au ranges between 0 to 100 K/nm, and can be contrasted to the values shown for Ag and Co, which have larger magnitudes.

Based on these results, we can justify why we did not observe deviations from the classical $\lambda \propto h^2$ spinodal behavior for Au, as evident from Fig. 2.1(g). Previous works have developed a theoretical framework to generalize the influence of thermocapillary forces on pulsed laser dewetting [185, 174]. The magnitude of attractive dispersion forces and thermal gradient forces [185, 174] can be incorporated into hydrodynamic models to obtain a final dewetting length scale described as:

$$\lambda = \sqrt{-\frac{16\pi^3\gamma}{A + 6\pi|\gamma_T|T_h h^3}}h^2, \quad (2.3)$$

where γ_T is the temperature coefficient of the surface tension. From above equation one can see that if the magnitude of the dispersive forces estimated by the term $(\frac{A}{2\pi h})$ is much larger then the thermal gradient forces given by $(\frac{3}{2}\gamma_T h T_h)$ one will continue to see the classical form of the spinodal dewetting. In Fig. 2.3(d) and (e) these two forces are calculated and compared for Gold and Cobalt respectively. It is clear that for Gold, the attractive dispersion forces are significantly stronger then the thermal gradient forces while in the case of Cobalt, the magnitude of attractive dispersion forces can be weaker then the thermal gradients. In Fig. 2.3(f) we have compared the experimentally determined length scales for Au, Ag, and Co and as evident, the Co behavior deviates from the classical h^2 behavior, while the ones for Au and Ag do not, implying a much weaker role of thermal gradient effects in these metals under ns pulsed laser dewetting. Another interesting observation that can be made with reference to Fig. 2.3(f) is that Au dewetting produces much smaller nanostructures then Ag or Co for a comparable film thickness. From the experimentally extracted values of the Hamaker coefficient, provided in Table 2.1, this appears to be due to the extremely large value of the Au Hamaker coefficient in conjunction with its weak thermocapillary effects .

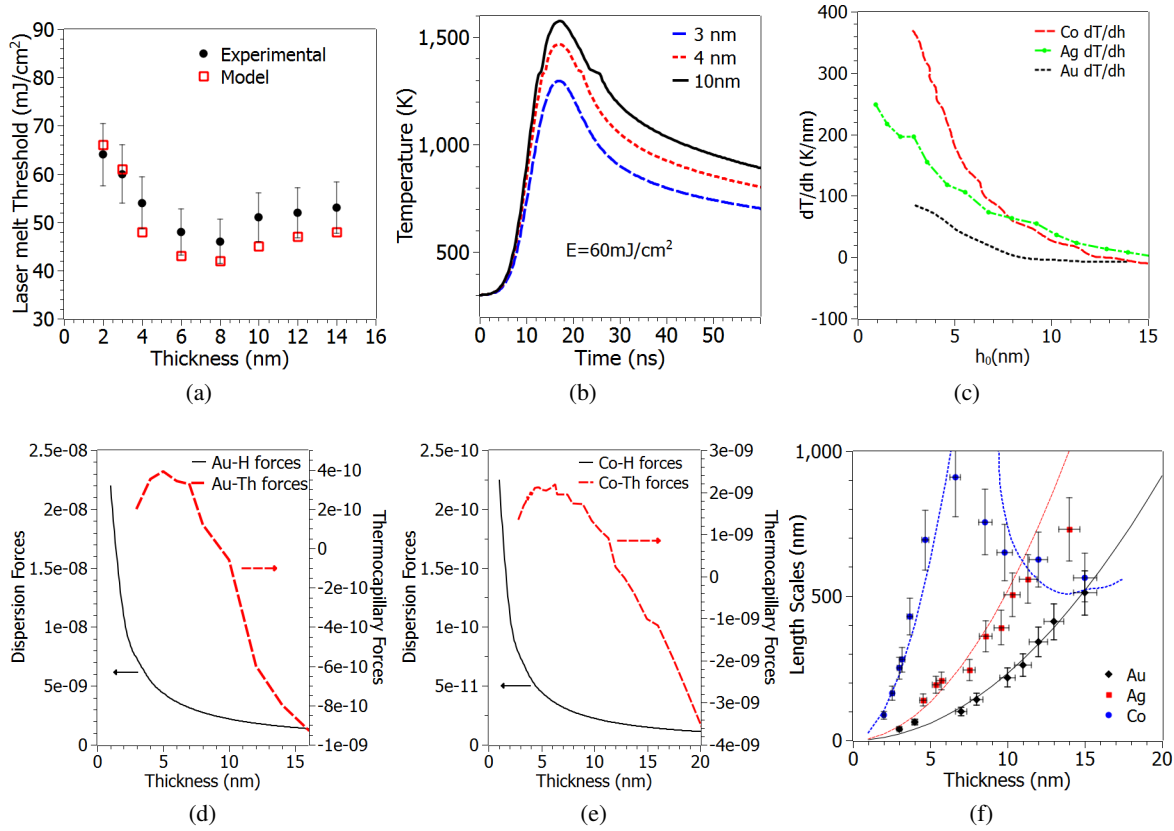


Figure 2.3: Thermal behavior of the Au film on SiO₂/Si irradiated by a pulsed laser (a) Laser energy density threshold for melting E₂ of Au films on SiO₂. Comparison of experimental measurements (closed symbols) with calculations (open symbols) using COMSOL Multiphysics [176]. (b) Time dependent temperature for two different Au film thickness at a fixed value of the laser energy density. (c) Theoretical estimates for the thermal gradients along the film vacuum interface following pulsed laser melting of Au films using a laser energy density of 70 mJ/cm². Data for Co and Ag films are also shown and were taken from ref. [184, 37]. (d) Thickness dependent magnitude of Au dispersion forces (Au-H) compared to thermocapillary forces (Au-Th) from the modeling results. (e) Thickness dependent magnitude of Co dispersion forces (Co-H) compared to thermocapillary forces (Co-Th) from the modeling results [37]. (f) Comparison of experimentally measured dewetting length scales of Au (this work), Co [36] and Ag [41]. The trend line equations are Au ($\lambda = 2.43 \times h^{1.98}$), Ag ($\lambda = 5.53 \times h^{1.97}$) and for Co in the spinodal regime and without thermal gradients is ($\lambda = 25.7 \times h^{1.98}$) while the thermal gradient effect was estimated from energy transfer model mentioned in [184].

2.3.5 Modeling

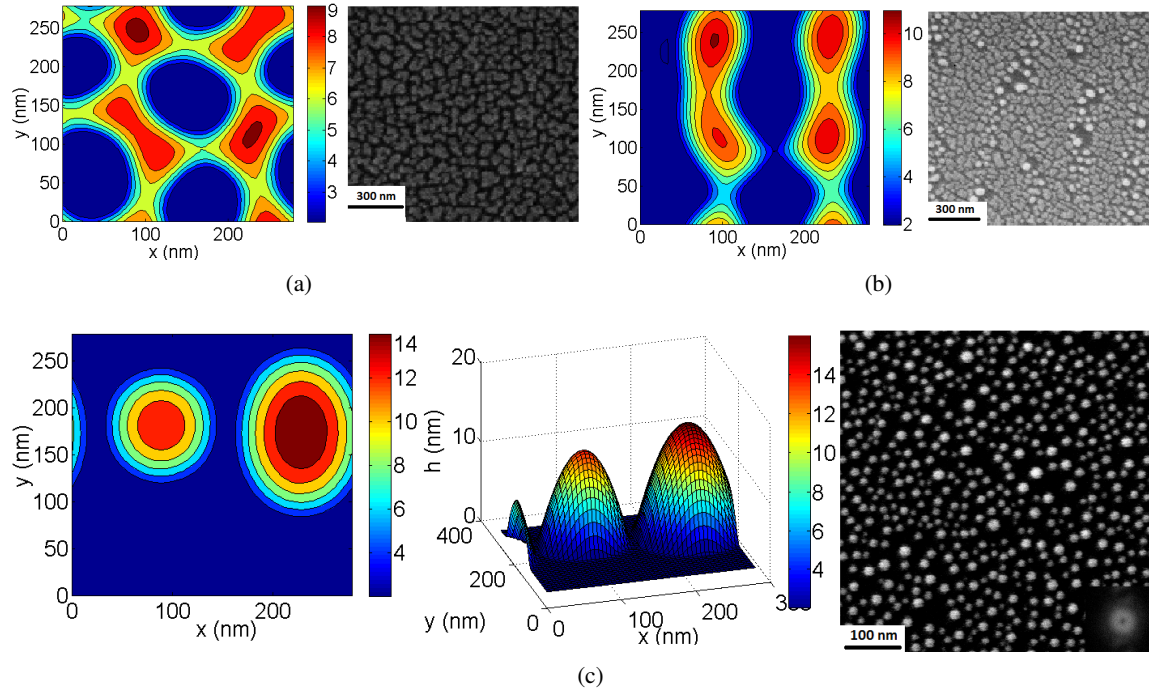


Figure 2.4: Three-dimensional (3D) modeling of the dewetting dynamics of a 5 nm Au film. (a) Contour plot of the height of the film at 560 ns compared to the SEM image of the film after 10 pulses. (b) Contour plot after 640 ns compared to the SEM image after 200 pulses. (c) Contour & 3D plots after 1200 ns compared to the SEM image of nanoparticles after 10500 pulses. The simulations were done with the Hamaker coefficient $A = 1.4 \times 10^{-18}$ J. Note the different scales in the modeling and experimental SEM figures.

Modeling the dynamics of the dewetting process that accurately captures the various physical effects, including the mass and thermal transport is highly important, since predictive computer-guided approaches are critical for the development of future nanomanufacturing scenarios. Here, a fully 3D and nonlinear modeling of Au film dewetting was performed, and the evolution of the morphology was tracked from the initial continuous film to the formation of nanoparticles. The full account of the transport models and numerical techniques has been published elsewhere [63, 65]. The models employed the thin film (lubrication) approximation of the nonlinear Navier-Stokes system of hydrodynamic equations, and incorporated the laser pulse-created, thickness-dependent temperature field in the energy equation and in the temperature-dependent surface tension. Simulations were done on a square domain of size 2λ (where λ is the length scale from the linear stability analysis of the thin film hydrodynamics describing spinodal dewetting) with periodic boundary conditions.

In Fig. 2.4(a), (b), and (c) the computed contour plots of the Au film height are shown at the different times for dewetting of 5 nm Au films. A Hamaker coefficient value of $A = 1.4 \times 10^{-18}$ J was used in the simulation. The contour plot and corresponding 3D plot are shown in Fig.2.4(c). It is evident from the early stage behavior that dewetting first results in a network of cells and then two ridges of roughly equal height

and width are formed by ripening. The cell network stage is consistent with the structure evidenced in the experiments, as shown by the SEM image in Fig. 2.4(a) for a Au film of 4.5 nm thickness following 10 pulses. Likewise, the later time stage, shown in Fig. 2.4(b), is consistent with the modeling structures of ridge-like or bicontinuous features. For later times, the evolution results in the break up of the ridges leading to the formation of nanoparticles, as shown in Fig. 2.4(c), and this compares well to the SEM image of the experimental state after approximately 10,500 pulses.

In this chapter we showed that Au dewetting is dominated by the internal Hamaker coefficient forces.

Chapter 3

Nanomaterials synthesis by a novel phenomenon: The nanoscale Rayleigh-Taylor instability

(Reported to AIP Advances, vol 4, 047116(2014))

3.1 Summary

The Rayleigh-Taylor (RT) interfacial instability has been attributed to physical phenomenon in a wide variety of macroscopic systems, including black holes, laser generated plasmas, and thick fluids. However, evidence for its existence in the nanoscale is lacking. Here we first show theoretically that this instability can occur in films with thickness negligible compared to the capillary length when they are heated rapidly inside a bulk fluid. Pressure gradients developed in the evaporated fluid region produce large forces causing the instability. Experiments were performed by melting Au films inside glycerol fluid by nanosecond laser pulses. The ensuing nanoparticles had highly monomodal size distributions. Importantly, the spacing of the nanoparticles was independent of the film thickness and could be tuned by the magnitude of the pressure gradients. Therefore, this instability can overcome some of the limitations of conventional thin self-organization techniques that rely on film thickness to control length scales.

3.2 Background

In the macroscopic or classical RT instability, a liquid film hanging on a substrate is destabilized when gravitational effects overcome the pressure exerted by the ambient atmosphere [88]. In this work we are primarily concerned with films whose thickness is substantially smaller than capillary lengths, which, for example, is of the order of 0.1 mm for the metal films we will investigate here. In this situation, gravity cannot play a role in stabilizing/destabilizing the film. Instead, other mechanisms to destabilize the films exist. One widely studied case pertains to the scenario when intermolecular attractive forces, such as dispersion forces, can overcome surface tension and result in spontaneous dewetting. This phenomenon has been widely investigated in organic and inorganic films in the context of spinodal dewetting and is typically exhibited by ultrathin films (normally <100 nm)[186, 37, 53, 57]. The characteristic feature of this instability is the strong dependence of the pattern length scale on the film thickness, i.e. $\lambda_{dew} \propto h_o^2$, where h_o is the initial film thickness [55, 36].

First, we describe a general scenario in which an RT-like instability can arise in nanometer thick films lying *on* a substrate, as shown in Fig.3.1(a). Picture a surface perturbation of the liquid film shown in Fig. 3.1(a) occurring into a hydrostatic pressure field where the pressure acting on the film is dependent on the local height of the film at any position x along the perturbed film, i.e. $p(h) = P(z, x)$. Two possible situations can be envisioned. In the first case, let the local pressure increase with increasing film height h . In this situation, the increased pressure will counter the growth of the perturbation (adding to the effect of surface tension) and therefore, increase the overall stability of the film to deformations. On the other hand, consider the case when the local $p(h)$ *decreases* with increasing h . In this case, the pressure field opposes the stabilizing effect of surface tension and, if it is large enough, can foster the growth of the perturbation, leading eventually to spatial and temporal behavior dependent on the various forces in play. Recently, two physical processes to achieve this type of scenario have been postulated. Bestehorn et al [187] suggested the theoretical possibility that a thin film on the underside of a substrate (i.e. RT unstable film) in equilibrium with its vapor phase under a steady-state thermal gradient can lead to patterns influenced by the evaporative process. A second possibility, a non-gravitationally generated RT instability, was reported as an experimental observation by Chen et al [188] in which the pulsed laser melting of a *bulk* Si surface immersed

of temperature of the gas phase, large transient gas pressures, that *fall* with distance away from the film, develop. This pressure gradient $P_Z = \frac{dP}{dz}$, with sign $P_Z < 0$, can produce a local film thickness-dependent gas pressure $P[x, T(z)]$ such that it drives the fluid to flow from regions of locally lower film thickness to higher ones, i.e. grows perturbations and produces the RT-like instability, as we demonstrate in the remainder of this manuscript.

3.3 Theory and modeling

The estimate of pressure gradients P_Z perpendicular to a film/gas boundary was evaluated with specific reference to the ns pulsed laser heating of a quartz/Au/Glycerol system irradiated by 266 nm wavelength laser light at normal incidence from the quartz side. At this wavelength, the photons are absorbed only by the Au film layer (and are transparent to quartz and Glycerol) [192]. The ensuing physical situation for laser energies of relevance here resulted in the melting of the Au film, as well as the formation of a gas phase region of Glycerol bounded by its fluid on one side and the molten Au film on the other, as shown in the schematic Fig. 3.1(a). First, a simple order of magnitude estimate (and sign) of the pressure gradient P_Z in the vapor was made by estimating a temperature gradient T_Z away from the film/gas interface through a thermal diffusion analysis as follows. For the T_Z in glycerol, we assumed that the spatial extent of the vaporized glycerol L_{gl}^v can be approximated as one thermal diffusion length, i.e. $L_{gl} = \sqrt{D_{gl}^{Th} \tau_p}$, where D_{gl}^{Th} and τ_p are the thermal diffusivity of liquid glycerol and the laser pulse time respectively. Using D_{gl}^{Th} of $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ from ref. [193], and using a laser pulse width of 9 ns, we get L_{gl} of $\sim 30 \text{ nm}$. The simplest approximation for the gradient is a linear one between the melting point of Au (1337.3 K) on the film side to boiling point of glycerol (563 K) on the glycerol vapor/fluid boundary side. This gives an order of magnitude for the thermal gradient, T_Z , as $\sim -25 \text{ K/nm}$, with the negative sign indicating that the temperature decreases in going from the interface into the Glycerol vapor/fluid region. Now, the $P_T = dP/dT$ for glycerol from P vs T empirical data available from standard references [193] varies with T and is $\sim 5 \times 10^6 \text{ Pa/K}$ at the melting point of Au. In other words the transient pressure gradient P_Z is estimated to be $\sim -1.25 \times 10^{17} \text{ Pa/m}$, and is a negative quantity, consistent with the sign of T_Z . Therefore, for a metal like Au with density of $\sim 20 \times 10^{-3} \text{ Kg} \cdot \text{m}^{-3}$, by using the dimensional equality of $|P_Z| = |\rho a| = |P_T \times T_Z|$, we get an extremely high acceleration value of $\sim 6 \times 10^{19} \text{ m}^2/\text{s}$, substantially larger than the estimates of Chen et al [188]. To better quantify this thermal effect, we performed finite element calculations to estimate the T_Z (and thereby P_Z) based on Fourier heat transport models for multilayer heating that incorporate phase change effects. We have previously developed these models in ref. [37, 63], where appropriate use of spatially and thermally varying materials parameters allowed us to successfully explain the thermal transport behavior in such nanoscale systems. The Fourier heat transport form of thermal transport was expressed as follows:

$$\rho C_p \frac{\partial T}{\partial t} = \nabla[k \nabla T] + Q_{laser}(z, t) \quad (3.1)$$

This equation was solved in each material layer, with ρ being the mass density of the layer, C_p the isobaric heat capacity, k the thermal conductivity, z the axis normal to the planar, fixed surface pointing from the substrate, as shown in Fig. 3.1(a), and $Q_{laser}(z, t)$ being the laser heating contribution given by $Q_{laser}(z, t) =$

$A(z)(1 - R(z))I(t)\exp[-A(z)z]$, where $R(z)$ is the thickness dependent reflectivity, and $A(z)$ is the thickness dependent absorption coefficient. $R(z)$ and $A(z)$ were calculated using the rigorous method described in Ref. [194]. The temperature dependent ρ , C_p and k for glycerol liquid and gas phase were calculated from Ref.[195] and for gold from [196]. The incident laser power was modeled as a Gaussian distribution with 9 ns pulse width, consistent with the characteristics of the laser used in the experiments to be described. Further details of the calculation are provided in Fig. 3.2.

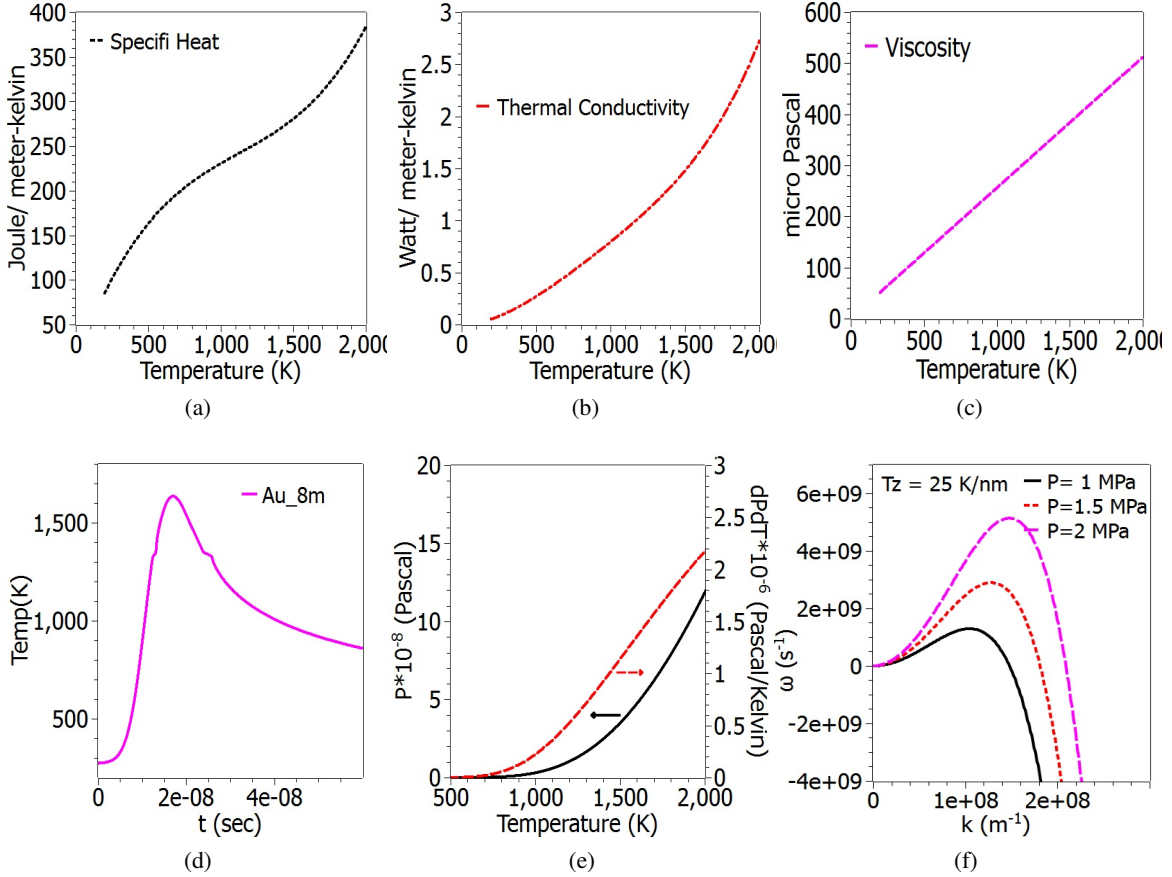


Figure 3.2: (a-c) Glycerol gas phase temperature-dependent quantities were calculated from Ref [195]. (d) Time dependent temperature for Au 8nm thick film at $62 \frac{mJ}{cm^2}$. (e) Pressure (P) and pressure gradient $\frac{dP}{dT}$, calculated using Clausius-Clapeyron equation and using available data in Ref [193]. (f) Plot of the growth rate vs wave number for the obtained dispersion relation at different pressures.

In Fig. 3.1(b), temperature vs distance behavior at the time corresponding to the peak temperature rise in a 8 nm thick Au film for various laser energy densities is shown. The large change in temperature with distance away from the film/gas interface (as well as film/substrate interface) is clearly evident and was calculated to be of the order of magnitude of 30 K/nm at the time of the peak temperature T^* . The gradients were estimated from these T vs distance plots as follows. A linear interpolation was applied between the position of the peak temperature at the film/gas interface to the position in the gas phase when the temperature dropped to the glycerol phase change temperature ($T=563$ K) . Using the empirically known

P vs T for glycerol [193], the effective pressure force, P_Z , was estimated for films of various thickness by selecting the laser energy density to achieve the same maximum temperature rise (of $T^* = 1750$ K). This result is shown by the dashed line in Fig. 3.1(c). The two important features are its large magnitude, i.e. $O(10^{16})\text{Pa/m}$, and the relative independence on the thickness of the film (for the same peak temperature T^*). As we discuss shortly, the magnitude of this P_Z force (in Pa/m or N/m^3) is substantially larger than other destabilizing forces, such as the intermolecular dispersion forces estimated for the quartz/Au system [196] and shown by the dotted line in Fig. 3.1(c).

To theoretically evaluate the role of this large P vs z on film behavior, we solved the mass transport dynamics using the thin-film hydrodynamic equation in the lubrication approximation of the Navier-Stokes equations [197]. This form allowed us to include the gas pressure in addition to the surface tension and dispersion forces due to intermolecular interactions that are already present in such ultrathin film on substrate systems, as depicted in Fig. 3.1(a) [56, 130]. The total Pressure $P(x, z)$ acting on the film at position x was expressed as the superposition of a disjoining pressure (Π), Laplace pressure P_L and pressure due to the gas layer $P[T(z(x))]$, as:

$$P(x, z) = P_L + \{\Pi(z) - \Pi(h(x))\} - P[T(z(x))] \quad (3.2)$$

We solved for the evolution of the instantaneous film height h in 1-dimensions (1D) by the mass conservation equation of the form

$$\frac{\partial h(x)}{\partial t} = -\frac{h^3}{3\mu} \frac{\partial}{\partial x} \frac{\partial}{\partial x} \left\{ \gamma \frac{\partial^2 h(x)}{\partial x^2} + \frac{d\Pi}{dh} \cdot h(x) + P[T(z(x))] \right\} \quad (3.3)$$

Where γ is the surface tension of the film-gas interface [γ_{GF} in Fig. 3.1(a)], η is the viscosity of the film, and the disjoining pressure Π for a thin film on substrate is given by $(\frac{A}{6\pi h_0^3})$, where A is the Hamaker coefficient. Since the local $P(x)$ is dependent on the temperature and the local height of the film, i.e. $P(x) = P[T(h(x))]$, its spatial derivative can be expressed as follows.

$$\frac{\partial P(x)}{\partial x} = \frac{dP}{dT} \frac{dT}{dz} \frac{\partial z(x)}{\partial x} = P_Z \frac{\partial z(x)}{\partial x}$$

Now since z is the coordinate measuring the height $h(x)$, we can express the 1st and 2nd order spatial derivatives of pressure as $P_Z \frac{\partial h(x)}{\partial x}$ and $P_Z \frac{\partial^2 h(x)}{\partial x^2}$, respectively, yielding an evolution equation of the form:

$$\frac{\partial h(x)}{\partial t} = -\frac{h^3}{3\mu} \frac{\partial}{\partial x} \frac{\partial}{\partial x} \left\{ \gamma \frac{\partial^2 h(x)}{\partial x^2} + \frac{d\Pi}{dh} \cdot h(x) \right\} - \frac{h^3}{3\mu} P_Z \frac{\partial^2 h(x)}{\partial x^2} \quad (3.4)$$

Here we ignored any contribution to film evolution resulting from the evaporation of the film material during the heating process. As shown in the Fig. 3.3, actual estimates of Au evaporation based on time and temperatures achieved here suggested negligible contributions. We also chose to ignore the dispersion force contributions, A_{VF} in Fig. 3.1(a), acting across the glycerol fluid/glycerol gas and glycerol gas/metal film interfaces. This can be justified due to the large thickness of the gas layer (~ 150 nm based on thermal model estimates) and partly due to the small values of A that typically exist across a gas medium. Therefore, the primary contribution came from the A_{VS} term in the dispersion forces. Equation 3.4 was solved using

linear stability analysis under boundary conditions of no slip at the film/substrate surface $v_z = 0$ at $z = 0$, and no shear stress ($\frac{\partial v_z(z=h)}{\partial x} = 0$) at the film/gas interface with sinusoidal perturbations of form $h(x) = h_o + \varepsilon \sin(kx) \cos(\omega t)$. This yielded a dispersion relation for deformation rate ω to wavevector k as:

$$\omega = \frac{h^3}{3\eta} [-\gamma k^4 - \Pi_h k^2 - P_Z k^2] \quad (3.5)$$

Where $\Pi_h = -\frac{A}{2\pi h^4}$, with the negative value signifying an attractive term, and the pressure gradient P_Z also has a negative sign, as explained earlier. From this, the characteristic wavelength $\lambda_{RT} = 2\pi/k_m$ was obtained from the maximum growth rate of perturbations k_m (i.e. $k_m^2 = \frac{-\Pi_h - P_Z}{2\gamma}$, when $\frac{d\omega}{dk} = 0$) as:

$$\lambda_{RT}^2 = \frac{8\pi^2 \gamma}{\frac{A}{2\pi h_o^4} - P_Z} \quad (3.6)$$

Also, the time scale $\tau_{RT} = \frac{2\pi}{\omega_m}$ associated with the growth of perturbations with wavelength λ was obtained by letting $k = k_m$ in Eq. 3.5, giving:

$$\tau_{RT} = \frac{6\pi\eta}{h_o^3(-\gamma k_m^4 - \Pi_h k_m^2 - P_Z k_m^2)} \quad (3.7)$$

The maximum evaporation rate as a function of temperature and its equilibrium vapor pressure can be expressed as [198] $T_e = 5.834 \times 10^{-2} P_e \sqrt{\frac{M}{T}}$. Where T_e = mass evaporation rate expressed in ($g - cm^{-2} - sec^{-1}$), M is the molecular weight, and P_e is the equilibrium vapor pressure in Torr. The above equation (1) can be conveniently expressed as the amount of material evaporation during the liquid life time T_l per pulse, in laser irradiation of a thin film. Typically the pulse width is fixed at 10 ns, but the liquid life time varies as a function of laser energy used for irradiation. Where ϕ is rate of material evaporation in ($cm/second$) is given as $\phi = \frac{T_e}{\rho}$, where (ρ) is density of the material ($g - cm^{-3}$). Where ϕ is rate of material evaporation in ($cm/second$). Laser irradiation of material above melt threshold results in T_l nanoseconds of liquid life time per pulse. Hence ϕ expressed in nm/s can be expressed as

$$\phi = \frac{T_e}{\rho} \times 10^{-2} \times T_l \quad (3.8)$$

3.4 Experiments

To analyze the implications of this model, experiments were performed for Au films (with thickness ranging from 4 to 12 nm) deposited on transparent bulk quartz (SiO_2) substrates, with this system immersed in a bulk glycerol liquid solution. The Au films were deposited in high vacuum ($\sim 1 \times 10^{-8}$ Torr) by electron beam deposition at room temperature onto commercially obtained, optical quality, SiO_2 substrates [36]. The deposition rate used here was typically ~ 1.5 nm/min as confirmed by atomic force microscope (AFM) step height measurements. Energy dispersive X-ray spectrometry (EDS) was used to measure the Au counts of the deposited films in a scanning electron microscope (SEM). The EDS counts were converted into an

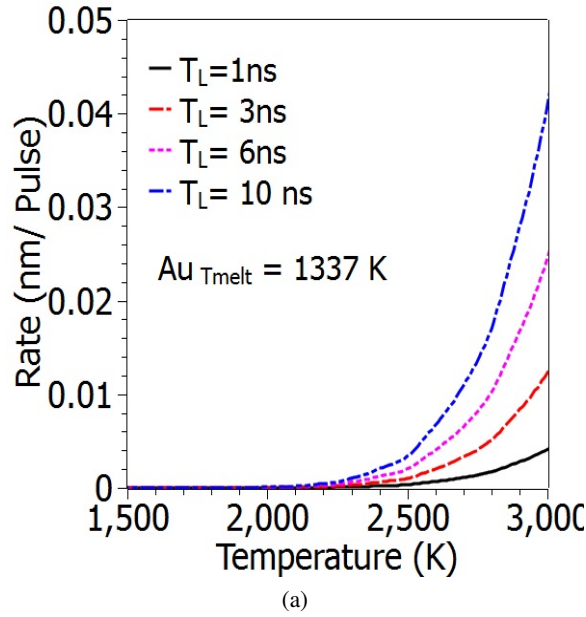


Figure 3.3: The rate of evaporation of Gold at different liquid life times.

equivalent thickness value by using calibration based on step-height measurements of the film thickness. Surface roughness of the deposited films were measured by AFM and established an upper limit of 0.5 ± 0.2 nm for the average root mean square (RMS) roughness over the entire thickness range. The Au/SiO_2 samples were positioned in a beaker filled with pure glycerol. Laser irradiation was performed at normal incidence from the quartz side, as depicted in Fig. 3.1(a), with an unfocused laser beam of area $1 \times 1 \text{ mm}^2$ at a repetition rate of 50 Hz for a total of 5000 pulses. Following the irradiation, the samples were removed from the fluid, dried in air, and the resulting nanostructures were investigated in a scanning electron microscope (SEM) as a function of film thickness h , and the laser energy density E .

3.5 Results and discussion

Fig.3.4 (a) shows an SEM image of the prototypical nanostructure obtained following the laser irradiation experiment, in this case for a 4 nm Au film (at 80 J/m^2 energy density). Nanoparticles with a well-defined inter-particle spacing and highly monomodal size distribution were obtained. The lower inset in the figure shows the fast fourier transform (FFT) of the contrast in the SEM images. The annular form of the FFT captures the spatial short range ordering typically prevalent in such thin film instabilities. The FFT analysis also allowed accurate calculations of the characteristic nanoparticle spacing. The particle size histogram (upper inset), showed that the standard deviation from the average size was less than 20%, consistent with the definition of a monomodal distribution used in chemical synthesis routes [199]. Such histograms allowed accurate determination of particle diameter.

One of the key implications of the theory (Eq. 3.6) is that when the magnitude of the thermal forces given by P_z are substantially larger than the dispersion forces ($A/2\pi h^4$) then the RT instability length scale

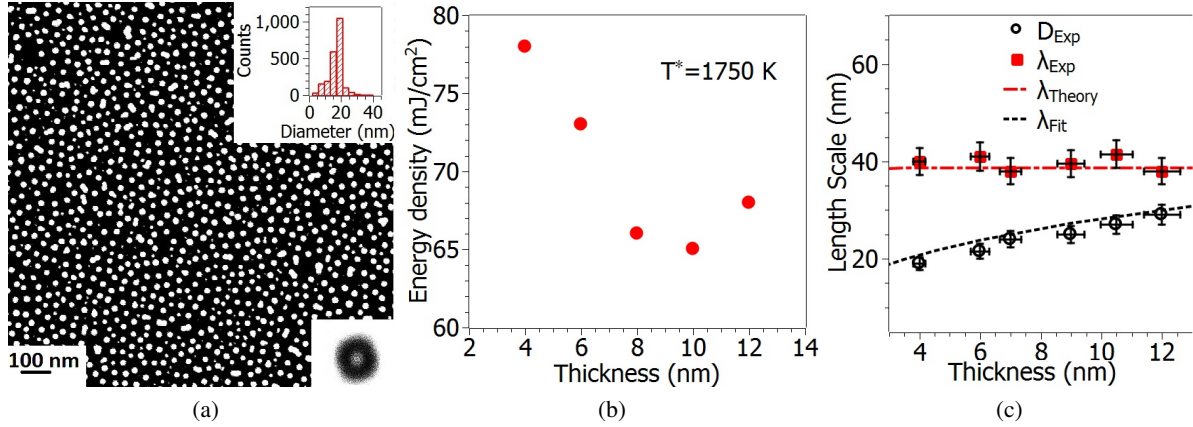


Figure 3.4: (a) SEM image of Au nanoparticles formed on quartz following pulsed laser melting of 4 nm Au film in glycerol fluid at $E=80 \frac{mJ}{cm^2}$. Top inset shows the monomodal size via the size histogram of the nanoparticles with diameter $D = 17 \pm 3$ nm. Bottom inset shows an annular FFT behavior of the contrast in the SEM image, indicating short range spatial order in the nanoparticle arrangement. (b) Thermal modeling predictions of the laser energy required to maintain the same peak temperature $T^* = 1750$ K in quartz/Au/glycerol systems with different Au film thickness. (c) Experimental measurements (symbols) vs theoretical predictions (lines) for the spacing (closed symbol) and diameter (open symbol) of nanoparticles as a function of film thickness.

should have no explicit dependence upon the film thickness. Indeed, as found by our thermal modeling calculations earlier, and depicted in Fig. 3.1(c), our experimental situation should be dominated by the P_Z forces, and hence the observed length scale should be explicitly independent of the film thickness and be given by:

$$\lambda_{RT} = 2\pi \sqrt{\frac{2\gamma}{-P_Z}} \quad (3.9)$$

To test this result, we performed experiments as a function of various Au film thickness by maintaining a similar magnitude of the P_Z forces. This was achieved by first obtaining a laser energy density that resulted in identical maximum temperature of $T^* = 1750$ K for the different thickness via thermal model calculations. This temperature was chosen for ease of experimental purposes. The modeling result to determine the laser energy density is shown in Fig. 3.4(b) (*this result was, in turn, used previously in Fig. 3.1(b) to generate the P_Z force values*). In Fig. 3.4(c) the experiment (closed symbols) and theory predictions (dashed line) for the nanoparticle spacing versus film thickness are shown for similar P_Z . Excellent agreement in trend and magnitude between theory prediction and experimental measurement is evident, strongly implying that the RT instability was responsible for the observed nanoparticles. In addition, the length scale was virtually independent of the film thickness, supporting the hypothesis of a classical RT-like instability.

In Fig. 3.4(c), the experiment (open symbols) and theory prediction (dotted line) for the nanoparticle diameter versus film thickness is also shown. If the initial volume of material is conserved during the laser irradiation process, the final diameter can be predicted from the characteristic length scales to be $D = c(\theta)(\lambda_{RT}^2 h)^{1/3}$ [37], where the constant $c(\theta)$ will be a function of the contact angle of the droplets. Using

a hemispherical particle size, which gives a diameter of $D = (\frac{3}{2}\lambda^2 h)^{1/3}$, excellent agreement in experiment and theory was found. Our thermal model calculations and the known temperature-dependent evaporation rate of Au also predicted extremely small material loss due to evaporation effects (result provided in the Fig. 3.3

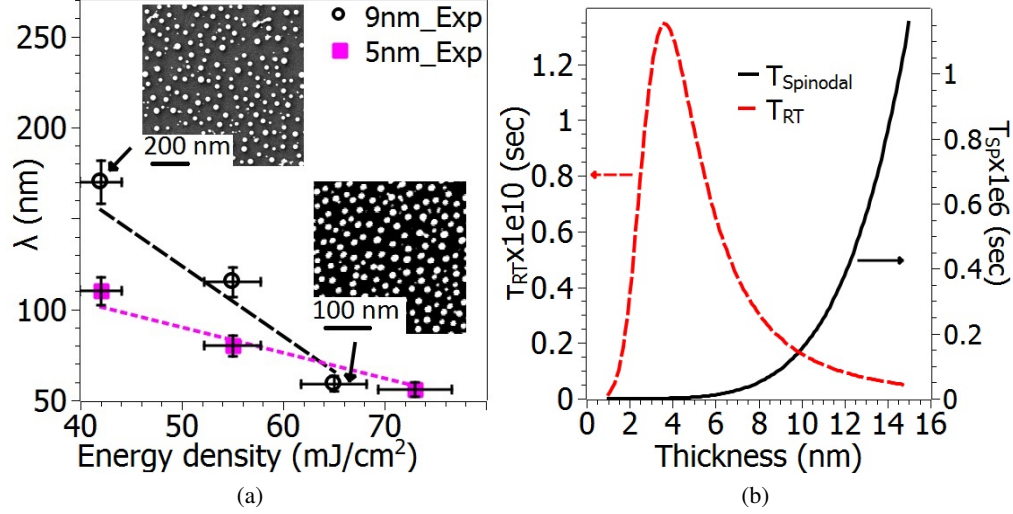


Figure 3.5: (a) Estimate of the RT instability time scale (left y-axis) as a function of film thickness for the experimental conditions used here. The order of magnitude is 10^{-10} s. In contrast, spinodal dewetting in such metal films is a much slower process (right y-axis) with time scales of order 10^{-6} s. (b) Nanoparticle spacing as a function of varying laser energy density for Au films of 9 (dashed line) and 5 nm (dotted line) films. Symbols show experimental measurements while the lines show theoretical predictions. The inset SEM images show the nanoparticle ordering for the 9 nm thick Au film at two different laser energies.

One of the well-known features of the classical RT instability is the appearance of hexagonal patterns during the early stages of deformation. In our experimental results, we are unable to capture these early stage features due to the extreme rapidity of the process. We estimated the time scales from Eq. 3.7 and found them to be of the order of $\sim O(10^{-10} - 10^{-11})$ sec for the various laser energy and film thickness conditions explored here, as shown in Fig. 3.5(a). Since this time scale is substantially smaller than the laser pulse width of 9 ns, therefore, it was only possible to observe the final ripened structures following destabilization of the film by the gas pressure driven RT instability process. From Fig. 3.5(a), it can also be noted that the RT instability time scale is much smaller than the spinodal dewetting time scale for all conditions investigated here, consistent with the much larger forces driving the RT instability effect. One of the interesting behaviors of the RT instability is the linear stability analysis prediction of a decrease in time scale with increasing film thickness. By assuming a negligible dispersion force, the RT instability time scale can be expressed as $\tau_{RT} = \frac{24\gamma\pi\eta}{h_o^3 P_z^2}$, which is in stark contrast to spinodal dewetting in which the linear time scale varies as $\tau \propto h_o^5$.

As shown in Eq. 3.9, the film thickness-independent result presented in Fig. 3.4(c) is a good indicator of the type of instability. However, practical implementation of this pressure-driven instability to potential

applications requires the flexibility in tuning spacing (and/or size) of the nanoparticles. This can be achieved by noting that varying the magnitude of P_Z can change the patterning length scales. From the thermal model result, Fig. 3.1(b), increasing laser energy density E increases the magnitude of the P_Z force due to the increased T_Z and this in turn should lead to a decrease in length scale through Eq. 3.9. This result is depicted in Fig.3.5(b) for measurements done on Au films of two different thickness. Clearly, increasing the laser energy density leads to substantial decrease in the nanoparticle spacings. In addition, the decreasing length scale predicted by theory calculations (dashed line) is in very good agreement with the experimental measurements (symbols).

In this chapter we discovered that pressure gradients generated by laser evaporation of bulk fluids in contact with a metal film can substantially modify the self-organization behavior.

Chapter 4

DC electric field induced phase array self-assembly of Au nanoparticles

(Reported to Nanotechnology, vol 25, 465301(2014))

4.1 Summary

In this work we report the discovery of phase array self-assembly, a new way to spontaneously make periodic arrangements of metal nanoparticles. An initially random arrangement of Gold (Au) nanoparticles on SiO_2/Si substrates was irradiated with linearly polarized (P) laser light in the presence of a DC electric (E) -field applied to the insulating substrate. For E-fields parallel to the laser polarization ($E \parallel P$), the resulting periodic ordering was single-crystal like with extremely low defect density and covered large macroscopic areas. The E-field appears to be modifying the phase between radiation scattered by the individual nanoparticles thus leading to enhanced interference effects. While phase array behavior is widely known in antenna technology, this is the first evidence that it can also aid in nanoscale self-assembly. These results provide a simple way to produce periodic metal nanoparticles over large areas.

4.2 Methods and techniques

Au films of thickness 10 ± 0.5 nm were deposited in high vacuum ($\sim 1 \times 10^{-8}$ Torr) by electron beam deposition at room temperature onto transparent square shaped (3×3 mm²) Quartz substrates as well as SiO_2/Si wafers consisting of optically smooth 400 nm thick thermally grown oxide layer on polished $\text{Si}(100)$ wafers. The wafers were cleaned in methanol, acetone, and DI water. The wafers were masked on their edges by a Cu tape (double sided 3M Cu conductive tape) prior to deposition. Following the deposition the tape was removed to leave behind the deposited film and bare substrate regions. The deposition rate used here was typically ~ 1.5 nm/min as confirmed by atomic force microscope (AFM) step height measurements of the film thickness. The surface roughness of the deposited films were measured by AFM and was established to be 0.5 ± 0.2 nm for the average root mean square (RMS) roughness.

The laser irradiation was performed in two stages. First, the deposited Au films were irradiated by a 266 nm ultraviolet laser having a pulse width of 9 ns. Irradiation was performed in air ambient and at normal incidence by an unfocused laser beam of area 1×1 mm² for 3000 pulses at a repetition rate of 50 Hz. The laser energy density used was $E = 60$ mJ/cm². This irradiation step resulted in a near-random distribution of Au nanoparticles due to the phenomenon of spinodal dewetting, which has been described in detail previously [200]. This stage 1 nanoparticle distribution was characterized by scanning electron microscopy (SEM) and is shown in Fig. 4.1(a). The Cu conductive tape was reapplied to the bare substrate regions prior to the stage 2 irradiation for application of the electric field. In stage 2, the Au nanoparticles on SiO_2/Si were irradiated with linearly polarized (P) laser light with an energy density $E = 90$ mJ/cm² in the presence of a DC electric field (E) applied to the SiO_2 layer, as shown in Fig. 4.1(b). The DC field was applied by a HP 6299A DC power supply connected to the Cu conductive tape. 3000 laser pulses were applied in this stage 2 irradiation, which was also performed in air ambient. Two different DC field orientations were investigated. In one case, the DC electric field (E) was applied parallel to the laser polarization (P), i.e. $E \parallel P$ as shown in 4.1 (b), while in the second case, the E field was orthogonal to the laser polarization, i.e. $E \perp P$. The quality of the patterns were subsequently investigated as a function of DC field strength between 0 to 90 Volts, in both orientations. The Au nanoparticles on Quartz, having identical characteristics of size and spacing as those prepared on the SiO_2/Si substrates, were used to measure the transmitted laser energy under application of DC E-fields. The transmitted energy was measured using an Ophir Electronics

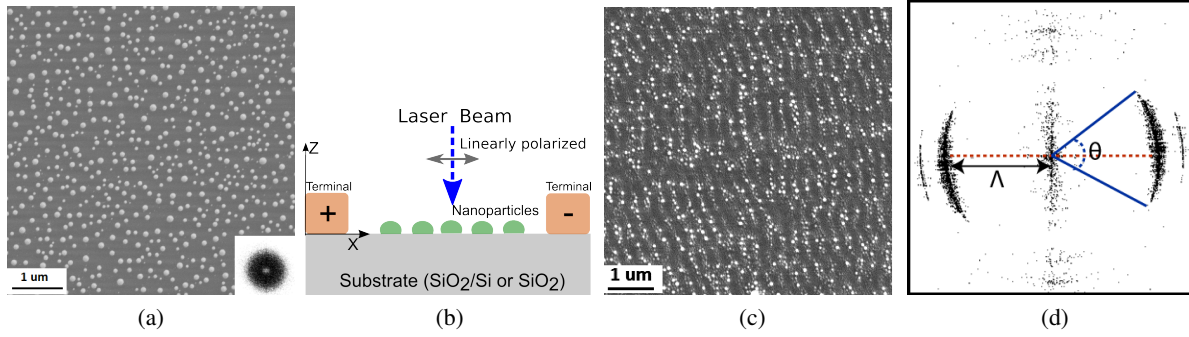


Figure 4.1: (a) SEM image of Au nanoparticles synthesized by pulsed laser dewetting at energy $E = 60 \frac{mJ}{cm^2}$. The inset shows the fast Fourier transform (FFT) of the image. (b) Schematic depiction of the experimental configuration of the DC electric field and the incident linearly polarized laser light. In the schematic shown the polarization and applied field are both along the x-direction, i.e. $E \parallel P$. In the $E \perp P$ the field was applied along the y-direction, which was perpendicular to the x-z plane shown. (c) SEM image showing domains of periodic structures misoriented with respect to each. This pattern was formed by irradiation of the nanoparticles in (a) by the laser with energy density of $90 \frac{mJ}{cm^2}$ and 0 V electric field. (d) Computer generated diffraction pattern (FFT) of the image in (c). The angular spread of the various domains (θ) and the spacing of the periodic pattern (Λ) was determined from such diffraction patterns.

PE30 A-P high power laser detector head with an Orion power meter. To determine the applicability of other materials, similar experiments were performed on Silver (Ag). The stage 1 Ag nanoparticles were prepared by spinodal dewetting at laser energy density $E = 60 \frac{mJ}{cm^2}$ from 8nm Ag film [201]. In stage 2, the Cu conductive tape was applied and Ag nanoparticles were irradiated with linearly polarized (P) laser light with an energy density $E = 90 \frac{mJ}{cm^2}$. Stage 2 experiments for Ag were performed at 0 Volts, 90 Volts using $E \parallel P$ & and 90 Volts using $E \perp P$ configurations.

High resolution surface imaging was performed using a ZEISS Merlin scanning electron microscope (SEM). AFM imaging was performed using Nanonics MultiView 1000 to analyze the 3D topography & quality of the resulting patterns. Zeiss Libra 200 MC transmission electron microscope (TEM) operating at 200 keV was used to determine elemental purity and crystallinity of the Au and Ag nanoparticles by performing High-angle annular dark field (HAADF) and bright field (BF) imaging, selected area diffraction (SAD) and electron energy-loss spectroscopy (EELS) studies. The cross-section TEM samples were prepared by using focused ion beam (FIB) technique in a Zeiss Auriga SEM with a Gallium beam operating at 30 kV. The Ga beam probe current used for cutting a lamella containing NPs was 2 nA which was gradually reduced to 200 pA during the sample preparation process. Following this, the final polishing to make electron transparent region was done by using 10 pA current and 30 kV accelerating voltage.

4.3 Results

Fig.4.1 (a) shows the short range ordered Au nanoparticles observed following the stage 1 laser irradiation on SiO_2/Si . The pulsed laser dewetting process [200] resulted in nanoparticles with a short-range

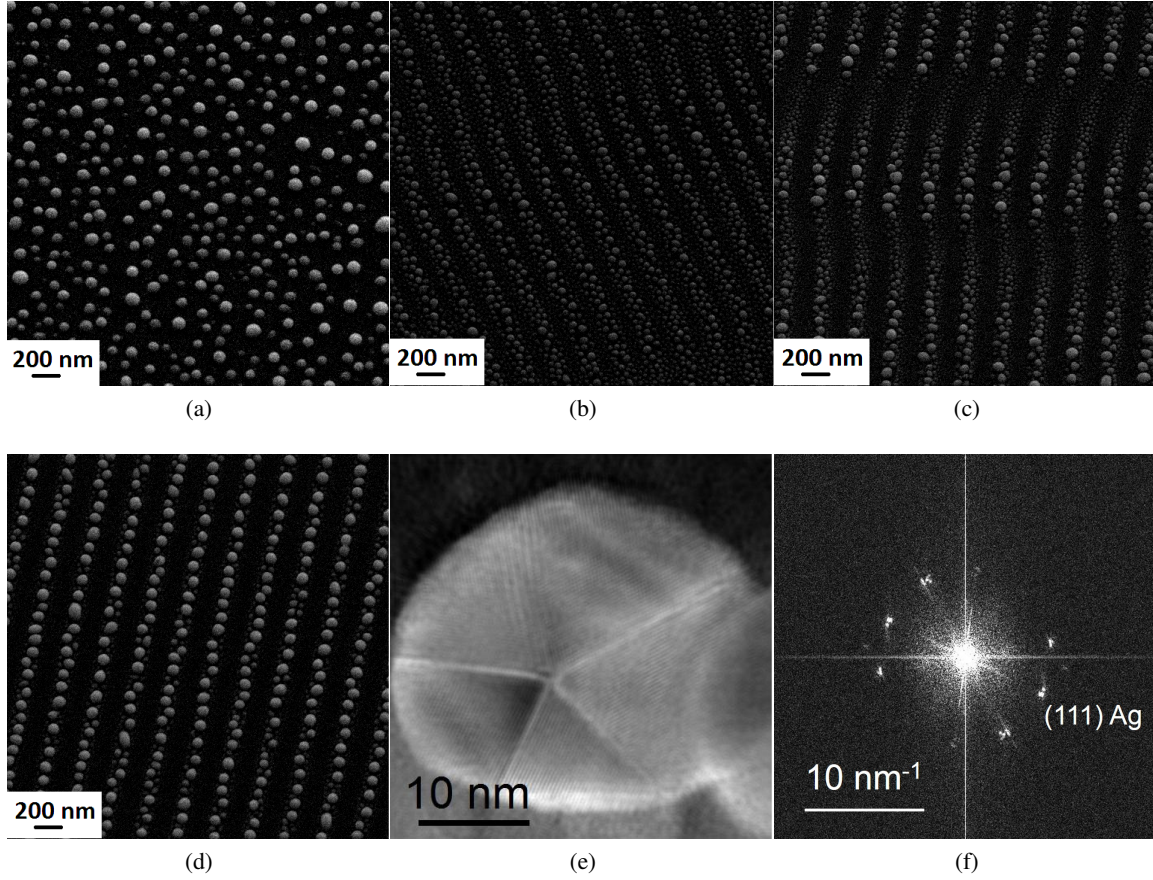


Figure 4.2: (a) SEM image of Ag nanoparticles synthesized by pulsed laser dewetting at energy $E = 60 \frac{mJ}{cm^2}$. (b) SEM image showing periodic structures of Ag formed by irradiation of the nanoparticles in (a) by laser energy density of $90 \frac{mJ}{cm^2}$ and 0 V electric field. (c-d) SEM images of Ag periodic structures formed from (a) by irradiating with laser energy density of $90 \frac{mJ}{cm^2}$ with $E \perp P$ and $E \parallel P$ at 90 Volts. (e) Fourier filter bright field image of Ag nanoparticle showing the presence of polycrystallinity (f) Diffraction spots from Silver nanoparticle shown in (e).

spatial order, as evident from the ring-like characteristic of the computer generated diffraction pattern [fast Fourier transform (FFT)] shown in the inset of Fig. 4.1(a). The short range ordered Au patterns were then irradiated with linearly polarized light in presence of a DC electric field applied to the substrate, as shown by the schematic Fig. 4.1(b). Fig. 4.1(c) show the LIPSS pattern formed when the nanoparticle array of Fig. 4.1(a) is irradiated with the higher laser energy density of $E = 90 \text{ mJ/cm}^2$, without any DC field. While a 1D pattern is evident, there are a large number of domains with slight misorientation in the direction of the 1D pattern. This rippled or wavy structure is reminiscent of the LIPSS patterns observed upon irradiation of bulk surfaces like Si, Ge, and Al by many authors [117, 118]. The extent of the disorder could be quantitatively represented by the angular spread of the diffraction pattern, as shown in Fig. 4.1(d). This diffraction pattern was also used to estimate the spacing Λ of the periodic features.

In Fig. 4.3(a-c), the patterns resulting from the $E \parallel P$ case for irradiation at 5, 50, and 90 V is shown. The angular spread in the orientation decreases substantially with increasing voltage, as evident from the SEM and the diffraction patterns (shown beside the SEMs). In fact, a single-crystal like spot diffraction pattern was evident at 90 V, signifying a very high quality of the 1D ordering.

In Fig. 4.3(d-f), the patterns resulting from the $E \perp P$ case for irradiation at 5, 50, and 90 V is shown. Once again an angular spread in the 1D orientations is evident from the SEM as well as from the arc-like nature of the diffraction patterns shown beside the SEMs. While the patterns again improved with increasing voltage, it started deteriorating after 50 volts.

To quantitatively compare the quality of the pattern, we measured the angular spread of the diffraction arcs for the various field orientations and magnitudes, and this is shown in Fig. 4.4(a). The angle was measured from the diffraction pattern, as shown in Fig. 4.1(d) using a built-in angle measuring tool in the open source ImageJ [202] software. From this comparison, two important features could be gleaned. First, the quality improved significantly with increasing voltage for the $E \parallel P$ case (closed symbols). This is clearly evident from the decrease in angular spread from 66° (at 0 V) to 8° at 90 V. Secondly, the $E \perp P$ case (open symbols) was very different from $E \parallel P$. While the angular spread decreased initially with increasing voltage, the disorder increased again beyond 50 V. We also observed that changing the voltage also changed the areal coverage of the pattern under the laser irradiation zone. In Fig. 4.4(b), Fig. 4.5(e-i) and Fig. 4.4(c), Fig. 4.5(c,d) we show representative large area SEM, AFM images comparing the 90 V cases for the $E \parallel P$ and $E \perp P$, respectively. Clearly, it is visually apparent that $E \parallel P$ case produces a very high quality 1D ordered pattern over very large areas as compared to the $E \perp P$ case. In Fig. 4.4(d), the area of coverage of patterns observed in the $E \parallel P$ case (closed symbol) increased with increasing voltage and was orders of magnitude larger than the 0 V case. On the other hand, for the $E \perp P$ case, the area coverage initially increased with increasing voltage, but subsequently dropped and was eventually of the same order of magnitude as the 0 V case. Even at its highest coverage at 50 V, the total area was more than an order of magnitude less than the final areal coverage achieved by the $E \parallel P$ case. Similarly, the second stage irradiation of Silver nanoparticles shows highest quality of patterns observed for $E \parallel P$ as shown in SEM image Fig. 4.2 (d) than at 0 V Fig. 4.2(b) or at 90 V in $E \perp P$ configuration shown in Fig. 4.2(c).

Fig. 4.5 (a-i) shows the AFM topography and corresponding 3D images of Au nanoparticles formed in stage 2. Fig. 4.5(a,b) show Au nanoparticles and 3D image at 0 V. Fig. 4.5(c,d) show the quality of patterns

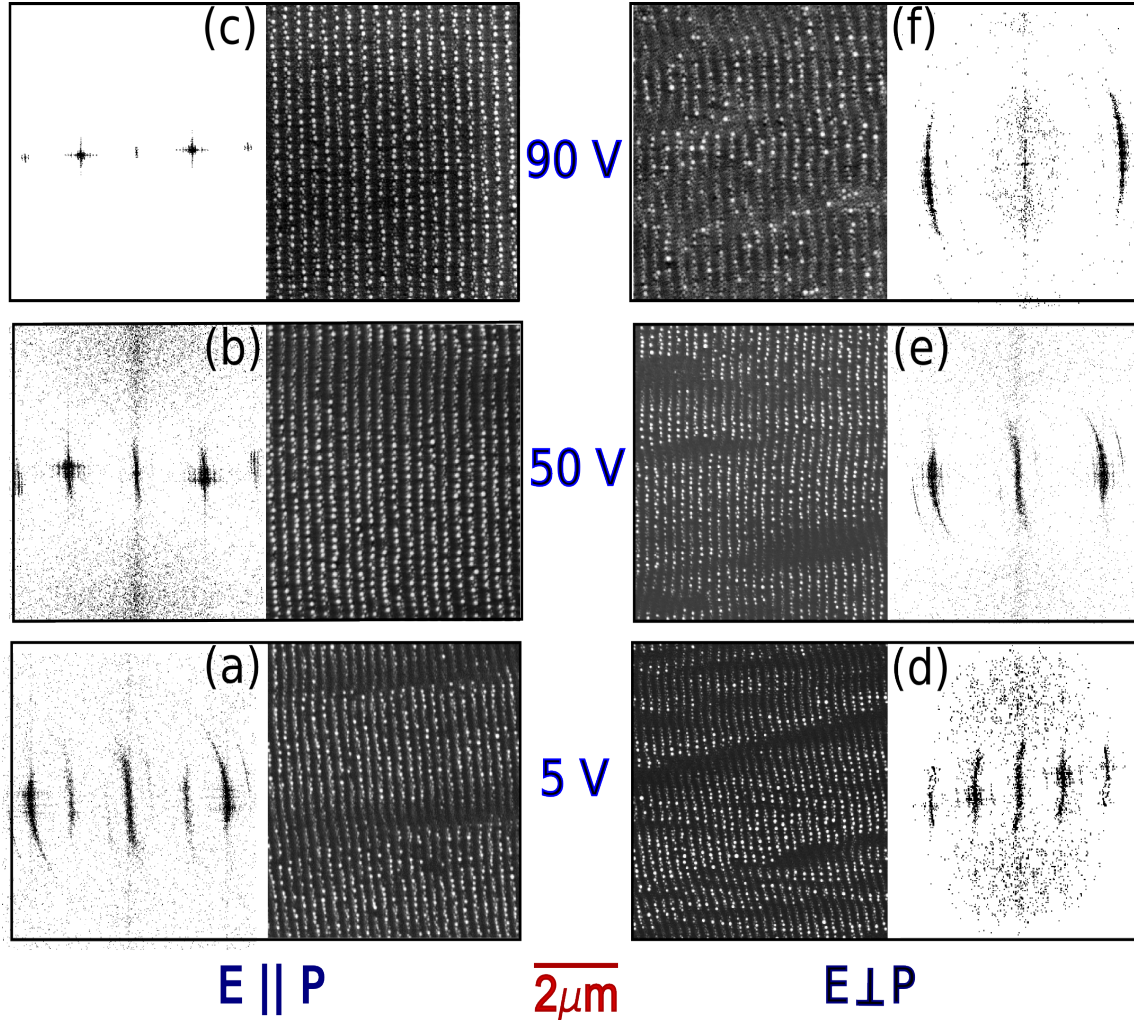


Figure 4.3: Result of irradiation of the nanoparticle state in Fig. 4.1(a) at laser energy $E = 90 \frac{\text{mJ}}{\text{cm}^2}$ in presence of DC electric fields of various voltages. (a-c) E-field parallel to polarization ($E \parallel P$) at 5, 50, 90 Volts, respectively. The corresponding FFT's are shown besides each SEM image. (d-f) E-field perpendicular to polarization ($E \perp P$) at 5, 50, 90 Volts, respectively. The corresponding FFT's are shown besides each SEM image. All images have the same scale bar, as shown.

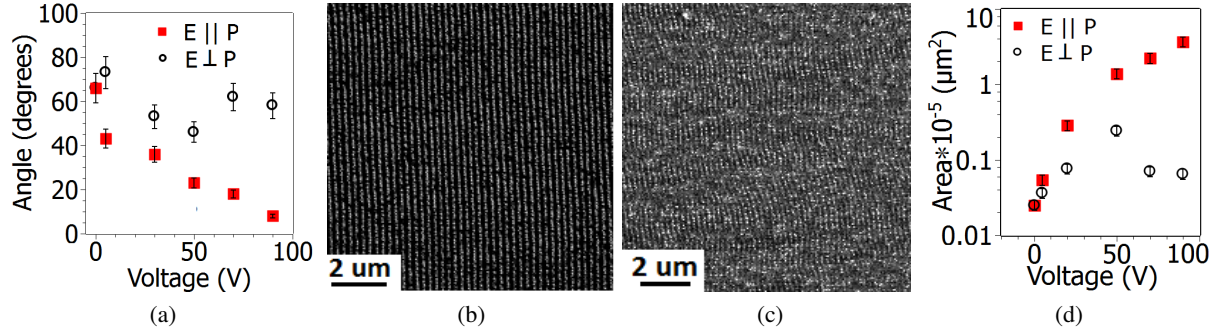


Figure 4.4: (a) Angular spread of the diffraction arcs as a function of the E-field voltage measured using the SEM images shown in Fig. 4.3. Closed symbols correspond to $E \parallel P$ while open symbols correspond to $E \perp P$. (b) Large area SEM image of the Au patterns from $E \parallel P$ at $E = 90 \frac{mJ}{cm^2}$. (c) Large area SEM image of of Au patterns from $E \perp P$ setup at $E = 90 \frac{mJ}{cm^2}$. (d) Area of coverage of the patterns on the sample surface as a function of applied voltage.

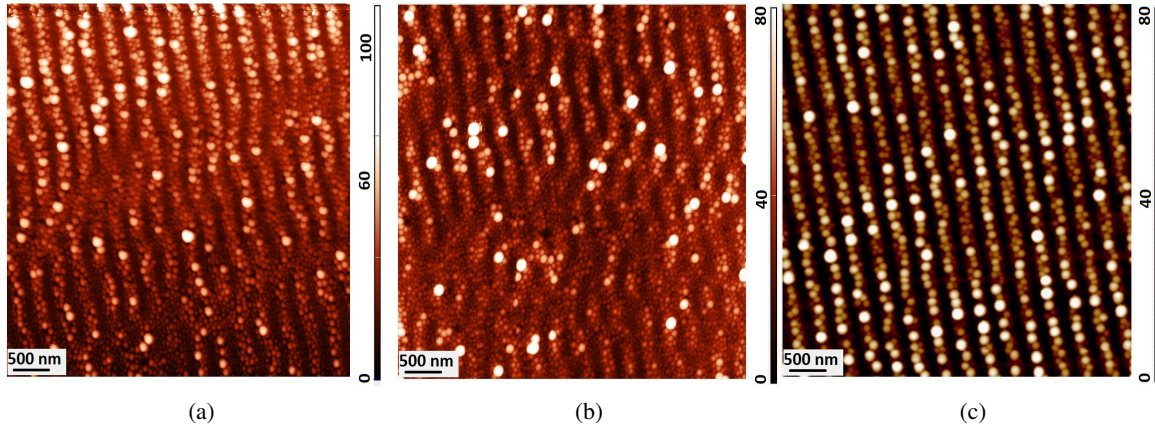


Figure 4.5: AFM topography images of Au periodic structures formed at laser energy densities $E=90 \frac{mJ}{cm^2}$ for various polarization and E-field cases. (a) 0 V. (b) $E \perp P$ at 90 V. (c) $E \parallel P$ at 90 V. The color bar is in units of nm.

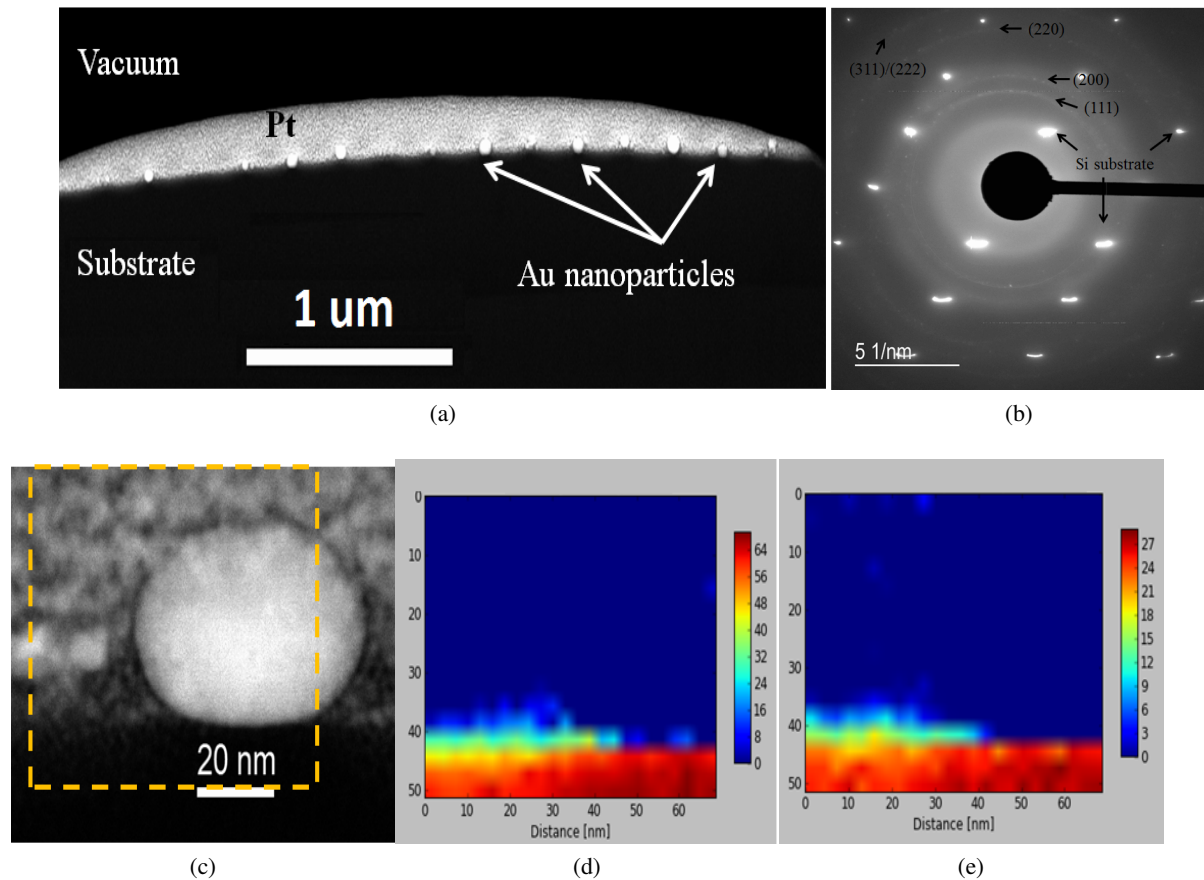


Figure 4.6: (a) Au nanoparticles on lamella prepared using focused ion beam (FIB) technique . (b) SAD pattern from lamella, rings are from Au and the bright spots are from the substrate. (c) HAADF image of Au nanoparticles on SiO_2 substrate showing contrast variation indicating polycrystallinity within the particle (d-e) TEM-EELS map of oxygen (O) and silicon (Si) in the Au nanoparticle.

at $E \perp P$ and 90 V. Fig. 4.5 (e-f) shows the Au high quality Au patterns formed from $E \parallel P$ at 90 V. Fig. 4.5 (g-h) show the large area high quality AFM scans for Au patterns formed for $E \parallel P$ at 90 V. Fig. 4.5 (i) show the line scan comparison of $E \parallel P$ and $E \perp P$ at 90 V. The important observation from the AFM images there is no reminiscent small particles between the rows and hence an evidence for high quality periodic arrangement for $E \parallel P$ case at 90 Volts. From the AFM images, for $E \perp P$ and 0 V, the patterns are of low quality with ripples and small reminiscent particles are present as clearly evident from the line scan in Fig. 4.5(i).

Since the NPs were undergone high energy irradiation during this process, it is important to perform the microstructural characterization. Fig.4.6(a-e) and 4.2 (e-f) shows TEM analysis of Au and Ag nanoparticles from high quality patterns obtained in $E \parallel P$. Fig.4.6(a,b) shows Au nanoparticles on lamella prepared using focused ion beam and the corresponding SAD pattern. The ring pattern with few bright spots in the Fig. 4.6(b) shows that the Au NPs are polycrystalline and some grains have preferred orientation corresponding to bright spots. The image shows the diffraction spots corresponding to (220), (200) and (111) planes which correspond to lattice planar spacing of 0.146 ± 0.001 , 0.205 ± 0.001 and 0.240 ± 0.001 nm respectively and is consistent with literature values for pure Au. Fig. 4.6 (d-e) shows the HAADF TEM image of Au nanoparticle and EELS maps for Silicon, Oxygen in the nanoparticle and we found that there is no inter atomic diffusion and the obtained Au nanoparticle is pure one. Similarly, Fig. 4.2(d) a fourier filtered bright field image of a Ag NP, which clearly shows the presence of polycrystallinity. To further verify whether synthesized NPs were pure or there is a possibility of atomic scale inter-diffusion of substrate material (SiO_2) with the Ag metal, FFT image from the shown NP was analyzed, as shown in Fig. 4.2 (f). The image shows the diffraction spots corresponding to (111) lattice plane and gives a lattice spacing of 0.237 ± 0.001 nm for the metal which is consistent with pure Ag one. These results suggest that NPs consist of pure Au and Ag metal even after re irradiated by laser energy density at $90 \frac{\text{mJ}}{\text{cm}^2}$. These results are similar to the ones shown earlier in the bimetallic NPs systems synthesized on various substrates by metal dewetting using relatively low laser energy [203, 47].

4.4 Discussion

The application of a DC electric field during the process of pattern formation has been studied almost exclusively for polymer thin film systems. Applying an external electric field to an initially continuous polymer film can give rise to modulations in surface tension, and charge density, leading to novel instabilities that can overcome the limitations encountered in conventional self assembly methods. Electric fields can also generate electrostatic stress at the polymer and air interface due to a mismatch in their dielectric constant, and this can lead to melt flows [204]. This phenomenon has been coined as Electrohydrodynamic (EHD) instability. By spatially varying the electric field, dynamic patterns with 1D and 2D symmetry as well as square, rectangular, and ring-like arrangements can be generated [205]. However, similar such studies of electric field induced instabilities and patterning of metals has not been explored so far. Furthermore, such E-field effects in the context of LIPSS phenomenon has also not been explored previously.

A quantitative theoretical approach to the 1D array formation under LIPSS requires solving the electrodynamic, heat, and kinetic equations in the presence of electric fields in three dimensions [206]. Rather than

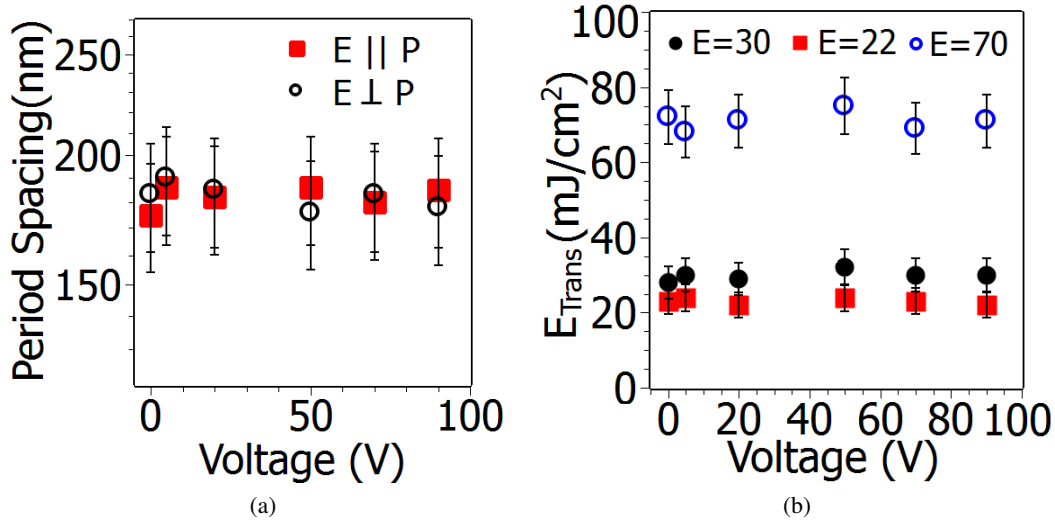


Figure 4.7: (a) The experimentally measured length scale of the periodic pattern as a function of voltage for the two orientations. (b) Transmitted energy of Au nanoparticles synthesized on transparent Quartz substrates for different incident laser energy densities for $E \parallel P$ ($E \perp P$ gave identical results and are not shown).

providing a quantitative explanation for this phenomenon, which will be the topic of a detailed presentation in the future, we hypothesize that the DC E-field influences the phase between the scattered radiation from the individual nanoparticles (dipoles), analogous to the phase array behavior seen in dipole antenna radiation [207, 208]. The remainder of our discussion is focused on building a case for this hypothesis.

First, we show that the periodic patterns are consistent with an interference phenomenon between the incident radiation and scattered light. From well-known LIPPS theory [206], the periodic spacing can be expressed as $\Lambda = \lambda / (n \pm \sin \theta)$, where λ is the wavelength of laser light (266 nm), n is the refractive index of the medium producing the scattering, and θ is the incident angle measured from the normal, and in our situation is 0° . Since the scattering process is occurring in the metal+substrate region, the effective refractive index will range between the value of pure Au ($n = 1.57$ at 266 nm) and SiO_2 ($n = 1.49$ nm at 266 nm) [209]. This suggests that the observed spacing should lie between ~ 169 to 179 nm. In Fig. 4.7(a) the experimentally measured value of Λ for the two orientations and various voltages was found to be unchanged within the experimental precision and was determined to be 182 ± 12 nm, quite close to the theoretical values predicted for LIPPS.

The second important evidence concerns the behavior of the periodic pattern as a function of voltage. From Fig. 4.1(c) and (d) one can claim that the arc-like behavior of the diffraction pattern is a result of small misorientations between various domains of 1D order. For the $E \parallel P$ case, increasing the voltage has the effect of aligning the various domains, hence changing the arc to a spot-like diffraction pattern, as seen from Fig.'s 4.3(a-c). The situation for $E \perp P$ is similar in that, again, the effect of voltage is to rotate the domains and modify the angular spread in the diffraction arcs. However, unlike the $E \parallel P$ case, a spot-like pattern is not achieved, and, in fact, at the higher voltages the misorientation begins to increase,

as evident from Fig. 4.3(b-e). A simple explanation for the improved ordering in the $E \parallel P$ case is an improvement in the interference quality as measured by the contrast function $CF = \frac{I_{max}-I_{min}}{I_{max}+I_{min}}$, where I_{max} and I_{min} represent the maximum and minimum in the interference intensity. If one considers as analogy a 2-beam interference between linearly-polarized plane waves defined by $E(r,t) = E_i \cos(k_i \cdot r - \omega t + \phi_i)$, where E_i is the amplitude, ω is the frequency, k_i is the wave vector, and ϕ_i is the phase, then the time averaged irradiance at any point on the surface is given by $I_T(r) = I_1 + I_2 + I_{12}$, with $I_i = \langle E_i^2 \rangle_t$ being the time averaged intensity of the individual components and the interference term I_{12} given by $I_{12} = \langle \vec{E}_1 \cdot \vec{E}_2 \rangle_t = 2\sqrt{I_1 I_2} \cos \delta$, where $\delta = k_1 \cdot r - k_2 \cdot r + \phi_i - \phi_j$ represents the phase difference that is ultimately responsible for the periodic modulation of the intensity. The two extreme conditions of interference are those of total constructive interference with $\delta = \pm 2m\pi$, and total destructive interference with $\delta = \pm 2(m + 1/2)\pi$, where m is an integer. For this 2-beam situation, the contrast function becomes $CF = \frac{2\sqrt{I_1 I_2}}{I_1 + I_2}$, implying that the only way to improve the interference quality is to either increase the magnitude of the interference function $\langle \vec{E}_1 \cdot \vec{E}_2 \rangle_t$ and/or decrease the magnitude of the denominator term.

One can recognize that the denominator of the contrast function is simply the sum of the total intensity in the incident light and scattered light. Since the incident laser light intensity is fixed, the only possible way to change this function is to modify the amount of light scattered by the nanoparticle + substrate system. To measure if such an effect can occur under the E-field, the total energy transmitted by the nanoparticle system, similar to that shown in Fig. 4.1(a), but prepared on a transparent Quartz substrate, was measured for various normal incidence laser energy densities between 25 and 70 mJ/cm². The result for the $E \parallel P$ is shown in Fig. 4.7(b) and it was evident that no change in transmitted energy occurred under the E-field, indicating that the amount of scattered energy was not changed by the E-field. Since the results were identical for the $E \perp P$ case, they are not shown. This result implied that the only way to improve the CF was to increase the magnitude of the function $\langle \vec{E}_1 \cdot \vec{E}_2 \rangle_t$.

Recognizing the nature of a dot product, the increase in $\langle \vec{E}_1 \cdot \vec{E}_2 \rangle_t$ can come by a better alignment of the electric field of the incident radiation with the scattered radiation. Since the incident electric field orientation is fixed by the laser polarization, the DC electric field must be influencing the orientation or magnitude of the scattered electric field along the polarization direction. This phenomenon can be explained by the principle of pattern multiplication used in phased array dipole antennas [207, 208]. The total scattered electric field vector will be a sum over the scattered field from each nanoparticle (dipole) on the surface. Assuming a collection of identical dipole radiators, the total electric field can be expressed as $E_2 = E_o f(\phi) AF(\phi, \Lambda, k_1, \beta)$, where E_o is the scattered electric field magnitude of each dipole (assumed identical here), $f(\phi)$ is a function representing the orientation of the scattered field, and AF is the array factor that represents the magnitude of pattern multiplication. The AF depends on ϕ , k_1 and Λ , but also depends on a phase difference β . In antenna design and operation, the magnitude of β can be adjusted such that the electric field or scattered radiation is maximized in a desired direction - a principle also used large area telescopes and radar systems. We suggest here, based on the experimental evidence provided above, that the role of the DC E-field is to modify β , the phase difference between the individual nanoparticle scatterers, thus modifying the interference CF. In the case of $E \parallel P$, increasing voltage has the effect of increasing the scattered field along the polarization direction thus leading to single-crystal like patterns. On the other hand, the $E \perp P$ seems to have the effect

of aligning the scattered field away from the incident polarization, this producing a poorer pattern quality. Our future work will focus on the fundamental reasons underlying the change in β with DC E-field.

In this chapter we discovered that a DC electric field applied to an insulating substrate modifies the scattering of light from nanoparticles leading to large range 1D ordered structures.

Chapter 5

Morphology Transitions in Bi-layer Spinodal Dewetting Systems

(Reported to Physical Review B, vol 85, 235446(2013))

5.1 Summary

In spontaneous pattern formation by spinodal dewetting, attractive intermolecular forces overcome surface tension and cause an ultrathin liquid film on a low energy substrate to produce ordered structures. Spinodal dewetting in single-layer film on a substrate, is usually manifested by an early stage surface deformation and a highly non-linear ripening stage that results in characteristic morphologies, typically bicontinuous- or hole-like states. Here we have experimentally constructed the dewetting morphology phase diagrams for a bi-layer (Ag, Co) liquid film system on SiO₂. Nanosecond pulsed laser melting was used to initiate and foster the dewetting as a function of film thickness and arrangement. The early stage ripening morphology was observed by scanning electron microscopy from which the phase diagrams were constructed. Unlike single-layer films, which only show one morphology transition between the bicontinuous to hole states as the film thickness is increased, the bi-layer system can have multiple transitions. We have utilized the thickness-dependent free energy curvature approach (Sharma and Khanna, Phys. Rev. Lett. 81 p3463 1998) to analyze the phase diagram. The location of the multiple transitions cannot be predicted from the curvature minima, as was the case for single-layer films. Nevertheless, despite the complexity from multiple interacting forces and different surface deformation mode in bi-layer systems, the phase diagram can be completely generated by knowledge of the free energy curvature of the respective single-layer films. These results can permit improved modeling of the non-linear dynamics in naturally driven self-organized phenomenon and help design nanomaterials for advanced applications.

5.2 Methods and techniques

5.2.1 Sample preparation

A detailed description of the preparation of bi-layer system made from Ag and Co on SiO₂ substrates has been published previously [42]. Briefly, ultrathin films of Ag and Co were deposited under ultrahigh vacuum ($\sim 1 \times 10^{-8}$ Torr) by electron beam evaporation (e-beam) and pulsed laser deposition (PLD) respectively, on commercially available and optically smooth 400 nm SiO₂ on Si(100) wafers. The deposition rates for each metal was typically 0.3 - 0.5 nm/min. Two type of bi-layer systems were investigated. In the AgCo system, a bottom Co film was deposited on the substrate, followed by the deposition of a top Ag layer, with total film thicknesses varying from 2 to 20 nm. For the CoAg system, a bottom Ag layer was deposited followed by deposition of the top layer Co film, with total thicknesses varying from 2 to 20 nm. Following the deposition, the films were irradiated in vacuum by a fixed number of pulses n (typically of order 10) from a 266 nm ultraviolet laser having a pulse width τ_p of 9 ns and a Gaussian spatial profile. Irradiation was at normal incidence with an unfocused laser beam of area $1 \times 1 \text{ mm}^2$ at a repetition rate of 50 Hz. The laser energy density was typically between 80 to 100 mJ/cm², and chosen such that the entire bilayer could be melted for all the thickness combinations, as evidenced by a visible morphology change [41, 36]. The morphology was studied as a function of the individual and combined film thickness of the bi-layer systems. The morphology was characterized using a Hitachi S-4300 scanning electron microscope (SEM).

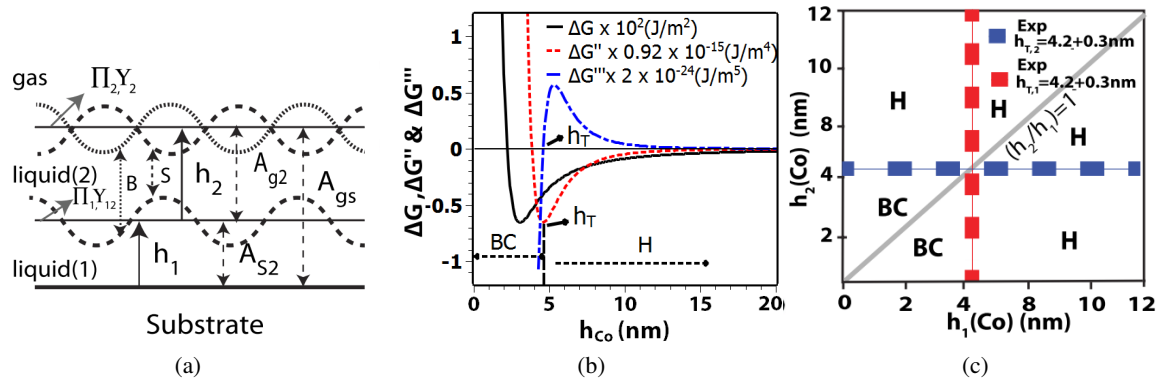


Figure 5.1: (a) Schematic description of the geometry and forces in a bi-layer dewetting system consisting of two liquids layers on the substrate. Also shown are the two possibly types of deformation modes: bending (B) and squeezing (S). The primary interaction forces include the Hamaker coefficients A_{ij} 's between the various pairs of interfaces and the interfacial tension at the film-vacuum and film-film interfaces. (b) The free energy of the Co/SiO₂ system (ΔG), its curvature ($\Delta^2 G$), and the third derivative ($\Delta^3 G$) are shown. The transition thickness h_T corresponds to the minima in the curvature or the zero in the third derivative [53]. (c) Experimentally constructed morphology phase diagram for a single-layer system of Co/SiO₂, which is identical to the bi-layer system of Co/Co on SiO₂. The dashed curves are drawn at the location of the morphology transition points for single-layer Co. The thickness of these lines represent the experimental uncertainty in measurement of the transition thickness. Various regions consisting of either bicontinuous (BC) or hole morphologies are shown.

Table 5.1: The various possible bi-layer cases based on the values of the individual film thickness and their relation to the single-layer transition thickness.

Case	bi-layer system specification	Case	bi-layer system specification
1	$(h_2 < h_1; h_2 < h_{T,2}; h_1 < h_{T,1})$	5	$(h_2 > h_1; h_2 < h_{T,2}; h_1 > h_{T,1})$
2	$(h_2 > h_1; h_2 < h_{T,2}; h_1 < h_{T,1})$	6	$(h_2 > h_1; h_2 > h_{T,2}; h_1 > h_{T,1})$
3	$(h_2 > h_1; h_2 > h_{T,2}; h_1 < h_{T,1})$	7	$(h_2 < h_1; h_2 > h_{T,2}; h_1 > h_{T,1})$
4	$(h_2 < h_1; h_2 < h_{T,2}; h_1 > h_{T,1})$	8	$(h_2 < h_1; h_2 > h_{T,2}; h_1 < h_{T,1})$

5.2.2 Morphology and transition observations

A typical bi-layer system is depicted in Fig. 5.1(a) with the various interfacial and dispersive intermolecular forces between the layers and the two general modes of deformations: bending (B) or squeezing (S). Based on the experimental observations from SEM imaging to be discussed shortly, the bi-layer systems could be classified into eight distinct cases, as shown in Table 5.1, on the basis of the thickness of the individual films in relation to each other and in relation to the single-layer transition thickness $h_{T,1}$ and $h_{T,2}$. As reported previously, the $h_{T,Co}$ for single-layer Co on SiO₂ is ~ 4 nm [37, 116], while the $h_{T,Ag}$ for Ag on SiO₂ film was found to be ~ 10.5 nm [41]. Guided by these experimental values, we evaluated the morphology for the two systems via SEM analysis as shown in Fig. 5.2, which denote the early-stage ripening morphology for different representative cases of the AgCo and CoAg bi-layer systems. Each SEM image was evaluated for the short range spatial order that is consistent with spinodal dewetting. This was done by obtaining the Fast Fourier Transform (FFT) of the SEM image contrast, which is shown in the inset of each SEM image. The FFT's showed the characteristic annular form, which is indicative of a narrow band of characteristic length scales for the height variations on the surface [129, 133, 210]. The primary information conveyed by this set of SEM images is the two distinctly different types of morphologies: the bicontinuous structures in Fig. 5.2(a,b, e and h) and the hole structures in Fig. 5.2(c, d, f and g), analogous to the situation with single-layer films [53, 41]. These were the only two observed bi-layer morphologies, besides a mixed state that comprised both morphologies which occurred when the bi-layer systems were at the positions of morphological transitions. In subsequent analysis and discussions we only distinguish between the type of patterns, i.e. BC or H. Any change between BC to H or vice-versa will be referred to as a phase transition, while any changes between similar morphologies but accompanied by a change in length scale of the pattern as film thickness was varied, was not considered as a phase transition (and is rather a pseudo-transition).

5.2.2.1 AgCo system

In Fig. 5.2(b) the early-stage morphology is shown for Ag(5nm)/Co(3nm) system in which both films are less than their individual transition thickness, corresponding to Case 2 in Table 5.1. The top Ag layer thickness was varied from $(4\text{ nm} < h_{Ag} < h_{T,Ag})$ on a bottom Co layer of 3 nm thickness. The morphology

progression is through formation of *bicontinuous* (BC) structures, which is the morphology behavior of single Silver or Cobalt layer on the substrate. In Fig. 5.2(d) the progression of morphology is shown for Ag(4nm)/Co(5nm) system in which the top Ag layer thickness varied from ($1 < h_{Ag} < 5\text{ nm}$) on a bottom Co layer of 5 nm, corresponding to Case 4 in Table 5.1. The morphology progression is through formation of *holes* (*H*), which is the morphology behavior of single Cobalt layer with $h_{Co} = 5\text{ nm}$ on the substrate. In Fig. 5.2(e) the progression of morphology is shown for the Ag(6nm)/Co(5nm) system in which top Ag layer thickness was varied from ($5\text{ nm} < h_{Ag} < h_{T,Ag}$) on a bottom Co 5 nm film, corresponding to Case 5 in Table 5.1. The morphology progression is through formation of *BC* structures which is the morphology behavior of single Silver layer on a substrate. In Fig. 5.2(f) the progression of morphology is shown for Ag(12nm)/Co(5nm) system in which both films are greater than their individual transition thickness, corresponding to Case 6 in Table 5.1. The top Ag layer thickness was varied as ($h_{Ag} > h_{T,Ag}$) on a bottom Co 5 nm film. The morphology progression is through formation of *H*, similar to the behavior of single Silver or Cobalt films on the substrate.

5.2.2.2 CoAg system

In Fig. 5.2(a) the progression of morphology is shown for the Co(4nm)/Ag(5nm) system, in which both films are less than their individual transition thickness. The top Co layer thickness was varied from ($1 < h_{Co} \leq h_{T,Co}$) on a bottom Ag layer of 5 nm thickness, corresponding to Case 1 in Table 5.1. The morphology progression is through formation of *BC* structures which is the morphology behavior of individual Silver or Cobalt layers on the substrate. In Fig. 5.2(c) the progression of morphology is shown for the Co(6nm)/Ag(5nm) system in which top Co layer of thickness $h_{Co} > 5\text{ nm}$ was deposited on a bottom Ag layer of 5 nm thickness, corresponding to Case 3 in Table 5.1. Now, the morphology progression is through formation of *H*, which is the behavior of single Cobalt layer with $h_{Co} > 5\text{ nm}$ on the substrate. In Fig. 5.2(g) the progression of morphology is shown for the Co(7nm)/Ag(12nm) system in which top Co layer was varied from $6\text{ nm} < h_{Co} < 13\text{ nm}$ on bottom Ag layer of 12 thickness, corresponding to Case 7 in Table 5.1. The morphology progression is through formation of *H*, which is the morphology progression of either film if they are greater than their transition thickness. In Fig. 5.2(h) the progression of morphology is shown for the Co(5nm)/Ag(8nm) system in which the top Co layer was varied as $5\text{ nm} < h_{Co} < 9\text{ nm}$ on bottom Ag layer of 9 nm thickness, corresponding to Case 8 in Table 5.1. The morphology progression is through formation of *BC structures* which is the morphology behavior of individual 9 nm Silver layer.

5.3 Discussion

From the collective SEM results of the early-stage morphology, a few general remarks can be made. A single transition is observed if the bottom layer is less than its transition thickness ($h_1 < h_{T,1}$) and the top layer is varied such that the thickness range includes the transition thickness $h_{T,2}$. In this system, the morphology transition from bicontinuous to holes occurs exactly at the top layer transition thickness i.e., at $h_{2,T}$. If

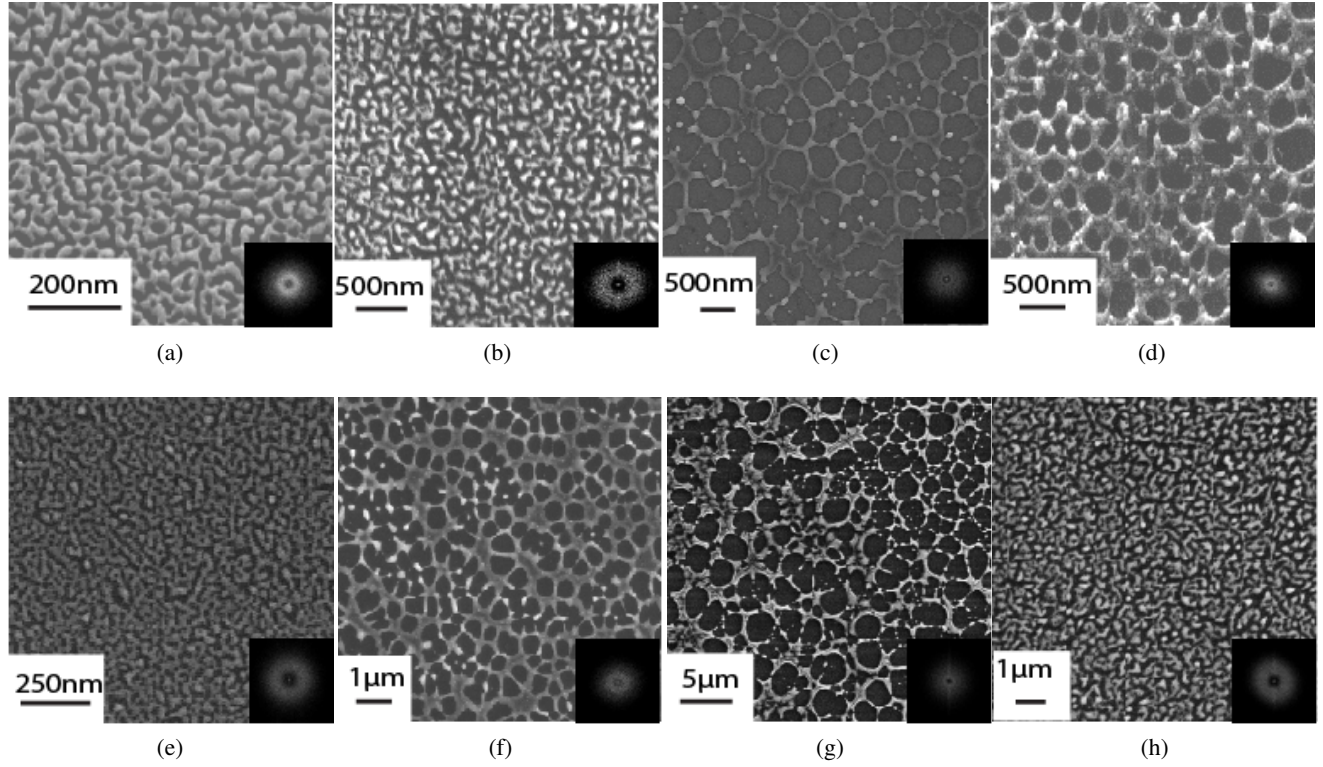


Figure 5.2: SEM images of the early stage spinodal dewetting morphologies in bi-layer dewetting systems. The film thickness from (a) to (h) corresponds to, (a) Co(4 nm)/Ag(5 nm) corresponds to Case 1, (b) Ag(5 nm)/Co(3 nm) corresponds to Case 2, (c) Co(6 nm)/Ag(5 nm) corresponds to Case 3, (d) Ag(4 nm)/Co(5 nm) corresponds to Case 4, (e) Ag(6 nm)/Co(5 nm) corresponds to Case 5, (f) Ag(12 nm)/Co(5 nm) corresponds to Case 6, (g) Co(7 nm)/Ag(12 nm) corresponds to Case 7, and (h) Co(5 nm)/Ag(8 nm) corresponds to Case 8. All cases are described in Table 5.1.

both layers of the bi-layer system were greater than their individual transition thickness, the progression of morphology is through *holes* and is evident from SEM images in Fig. 5.2(f & g). On the other hand, if both layers were less than their transition thickness the progression of morphology is through bicontinuous structures and is evident from SEM image in Fig. 5.2(b). Finally, if both films were of equal thickness and if one film is greater than its transition thickness, a combination of holes and bicontinuous structures was observed. On the other hand, multiple morphology transitions are observed when $h_1 > h_{T,1}$ and $h_{2,T} > h_{T,1}$, and the top layer is varied as $(1 < h_2 < h_{2,max})$, where $h_{2,max} > h_{T,2}$. In other words, here the morphology progression will begin with holes for $h_2 < h_1$, transition to bicontinuous structures at $h_1 < h_2 < h_{T,2}$, and then transition to holes at $h_2 = h_{T,2}$. This feature can be observed in the AgCo system, since $(h_{Ag,T} > h_{Co,T})$ and is evident from the SEM images in Fig. 5.2(d-f). Based on these results, we have constructed the bi-layer phase diagram, discussed next.

5.3.1 Construction of bi-layer phase diagram

The experimentally constructed phase diagram for the AgCo is shown in Fig. 5.3(a) and for the CoAg system in Fig. 5.3(b). The phase diagram identifies the morphology for any given combination of h_1 and h_2 . Individual regions in the diagram are bounded by values of the experimental transition points $h_{T,1}^{Expt}$, $h_{T,2}^{Expt}$, the film thickness ratio line with slope 1 (i.e. $h_2/h_1 = 1$) and the two thickness axis. This construction permits one to easily predict the early stage morphology for any given path and for any given individual thickness of the components of the bi-layer system and their arrangement. For instance, in Fig. 5.3(a), for the AgCo system, a vertical dashed line drawn is drawn beginning at the bottom layer thickness $h_1 = h_{Co} = 5$ nm and represents the case where the top layer thickness of the bi-layer system is varied for a constant bottom layer. For the various positions along this path, the morphology as well as morphology transitions can readily be identified. For instance, in this case, a first morphology transition will occur at the location of the intersection of the line with the $h_2/h_1 = 1$ line and then a second transition will occur at the intersection with the $h_{T,2}$ line. An important result here was that the experimentally observed locations of the transitions, i.e. $h_{T,1}^{Expt}$ and $h_{T,2}^{Expt}$ coincided within experimental uncertainty to the transition thickness of the respective single-layer films, in this case Co and Ag respectively. It should be re-emphasized here that we refer to a phase transition only when there is a change in the type of morphology, i.e. BC and H. There are several examples where there can be a change in the length scale of any given morphology, such as the BC or H, when one of the boundaries is crossed. For instance, in Fig. 5.3(a), there is a change in length scale in going from the Case 1 (marked as C1 on the figure) region to the Case 2 (C2) region. However, this transition is not a phase transition, and instead, one can refer to it as a pseudo-phase transition.

In similar fashion, in Fig. 5.3(b), for the CoAg system, a line drawn at $h_2 = h_{Co} = 5$ nm and horizontal to the h_1 axis is shown and represents the case where the bottom layer thickness of the bi-layer system is varied with a constant top layer. In this example, again multiple transition are evident at the intersections with the $h_2/h_1 = 1$ line and then with the $h_{T,1}$ position. Once again the experimentally observed locations of the phase transitions coincided within experimental uncertainty to the transition thickness of the respective single-layer systems. Finally, for completeness, we have also constructed the phase diagram for a single-

layer, which can be thought of as a bi-layer with identical liquids, such as Co/Co, in Fig. 5.1(c). One significant difference in the single-layer behavior over the bi-layer case is that only a single morphology transition is possible for any path in the single-layer system.

5.3.2 Free energy analysis

In the context of spinodal dewetting, the thickness-dependent free energy $\Delta G(h)$ plays two roles. First, it establishes the “spinodal” nature, i.e. the film thickness range over which the curvature ($\Delta^2 G = \frac{d^2 \Delta G}{dh^2}$) is negative, analogous to spinodal phase segregation. When this condition is satisfied, it is then possible to extract the characteristic length scale of the spinodal system via a linear analysis [57]. Second, as was first shown by Sharma and Khanna [53], the position of the curvature minima, i.e. where $\Delta^3 G = \frac{d^3 \Delta G}{dh^3} = 0$, identified the location of the transition thickness h_T for single-layer spinodal dewetting. They observed also that bicontinuous structures appear in films whose initial thickness lie to the left of the curvature minimum h_T , while holes correspond to films with thickness to the right of the minimum. This feature has been subsequently verified in single-layer polymer [54, 135] and in single-layer metallic films [41, 136]. The underlying physical reasoning of this finding was attributed to the role of the third derivative of the free energy in the mass transport behavior of the film. Based on this curvature argument, we have analyzed the single-layer and bi-layer free energies and their derivatives next.

5.3.2.1 Single-layer free energy

Thin film wetting and dewetting behavior is partly determined by the disjoining pressure, which arises from the interaction energies of molecules in a film, which are in close proximity to a surface or interface, being different from that in the bulk. The total disjoining pressure can be written as a combination of long range (Π_l) forces, for example the van der Waals force, and short range (Π_s) interactions such as from electrostatic double layers, polar hydrophobic, and other short range repulsions [211, 177]. For single-layer metal films, we have previously estimated a total disjoining pressure by considering a long-range attraction, a short-range repulsion expressed as a Lennard-Jones type, and a short range electrostatic force given by [41]:

$$\Pi(h) = \frac{A}{h_c^3} \left[\left(\frac{h_c}{h} \right)^3 - \frac{1}{3} \left(\frac{h_c}{h} \right)^9 \right] + \frac{S^p}{l} \exp\left(-\frac{h}{l}\right) \quad (5.1)$$

where A is Hamaker coefficient, l is the correlation length, S^p is the spreading coefficient, θ is the equilibrium contact angle of the film on the substrate, and h_c is defined as $\frac{A}{h_c^3} \frac{3^{4/3}}{8} = -2\gamma \sin^2(\theta/2)$, where γ is the surface energy of film vacuum interface. Using Eq. 5.1, the bilayer h_T is calculated from the position of the minimum of free energy curvature ($\frac{d^2 \Delta G}{dh^2}$) or where $\frac{d^3 \Delta G}{dh^3} = 0$, which is expressed as:

$$\frac{d^3 \Delta G}{dh^3} = -\frac{12A}{h^5} + \frac{30Ah_c^6}{h^{11}} - \frac{S^p}{l^3} \exp(-h/l) = 0 \quad (5.2)$$

The above analysis was performed for Co films on an SiO₂ surface (with the various parameters shown

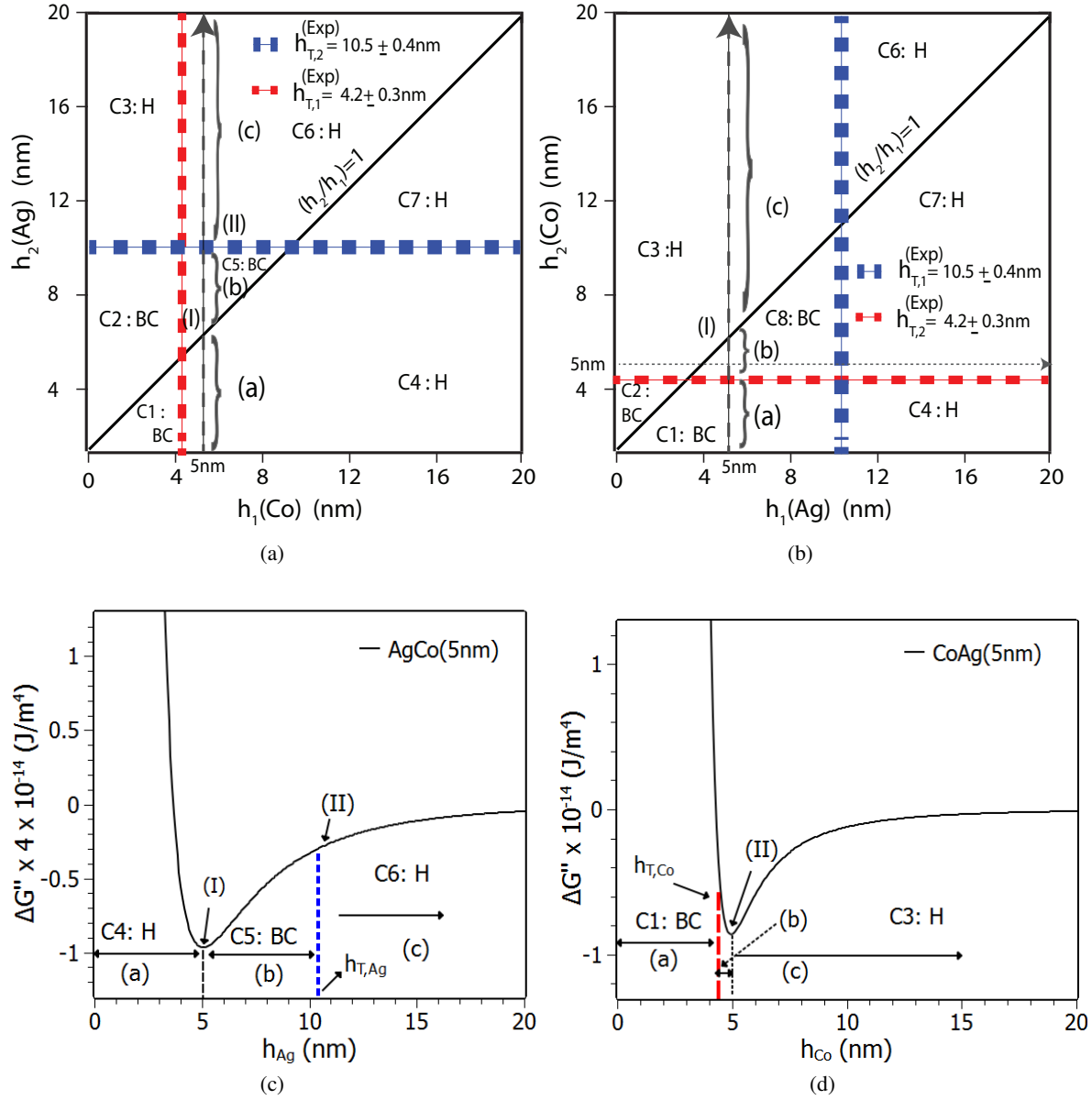


Figure 5.3: (a) Experimentally generated morphology phase diagram of AgCo system ($h_{T,2} > h_{T,1}$). (b) Phase diagram of CoAg system ($h_{T,2} < h_{T,1}$). (c) Free energy curvature of bi-layer AgCo(5 nm) where the red and blue lines corresponds to individual Co and Ag transitions. (d) Free energy curvature of CoAg(5 nm) where red and blue lines corresponds to individual Co and Ag transitions. The width of the experimentally observed transition lines in Fig. (a) and (b) corresponds to the uncertainty in film thickness measurements.

in Table 5.2) and the result is shown in Fig. 5.1(c). The transition thickness h_T is shown at the position where $\frac{d^3\Delta G}{d^3h} = 0$. Experimentally, we observed bicontinuous structures to the left of h_T and holes on the right of the transition thickness and the resulting Co single-layer phase diagram was of the form shown in Fig. 5.1(c).

5.3.2.2 Bi-layer System free energy

In order to verify if the morphology phase diagram for the bi-layer can also be addressed by the curvature-dependent behavior, we also performed the free energy analysis for the bi-layer films. The disjoining pressures acting across the liquid-liquid interface $\Pi_1(h_1, h_2)$ and liquid-gas interface $\Pi_2(h_1, h_2)$ can be computed from the forces acting at the interfaces [139] along with short range forces represented as an exponential decay [137, 177, 212] as follows:

$$\Pi_1(h_1, h_2) = \frac{A_{s2}}{6\pi h_1^3} - \frac{A_{g1}}{6\pi(h_2 - h_1)^3} - \frac{S_{1s2}^{s.r}}{l} \exp\left(\frac{d_0 - h_1}{l}\right) \quad (5.3)$$

$$\Pi_2(h_1, h_2) = \frac{A_{sg} - A_{s2} - A_{g1}}{6\pi h_2^3} + \frac{A_{g1}}{6\pi(h_2 - h_1)^3} - \frac{S_{21}^{s.r}}{l} \exp\left(\frac{d_0 - (h_2 - h_1)}{l}\right) \quad (5.4)$$

The thickness-dependent free energy for the bi-layer can now be expressed as:

$$\Delta G(h_1, h_2) = \frac{A_{sg} - A_{s2} - A_{g1}}{12\pi h_2^2} + \frac{A_{s2}}{12\pi h_1^2} + \frac{A_{g1}}{12\pi(h_2 - h_1)^2} - \frac{S_{1s2}^{s.r}}{l} \exp\left(\frac{d_0 - h_1}{l}\right) - \frac{S_{21}^{s.r}}{l} \exp\left(\frac{d_0 - (h_2 - h_1)}{l}\right) \quad (5.5)$$

Here, A_{gs} , A_{s2} , and A_{g1} are the Hamaker coefficients of gas and substrate, substrate and liquid, gas and liquid 1 pair of interfaces, as shown in Fig. 5.1(a), l is the correlation (or Debye) length, which is typically in the range of 0.2-1.0 nm [213, 177], d_0 is the equilibrium cut off distance taken as 0.158 nm [213, 177], and $S_{1s2}^{s.r}$ and $S_{21}^{s.r}$ are the short range part of the spreading coefficients. These are also related to the total spreading parameter S of the interface according to Eq. 4 in Reference [214] as:

$$S = S^{vdw} + S^{s.r}$$

where S^{vdw} represents the van der Waals component of spreading coefficient, connected to the effective Hamaker constant via $S^{vdw} = \frac{-A_{effective}}{12\pi d_0^2}$. Hence

$$S_{1s2} = S_{1s2}^{vdw} + S_{1s2}^{s.r} \equiv -\frac{A_{effective}}{12\pi d_0^2} + S_{1s2}^{s.r} \quad (5.6)$$

Similarly, $S_{21}^{s.r}$ was calculated for both AgCo and CoAg and the bulk spreading coefficients, S_{1s2} and $A_{effective}$, were calculated from Ref. [138]. The various parameters used for the bi-layer free energy analysis are shown in Table 5.2. Analogous to the single-layer, free energy curvature, was estimated from Eq. 5.7. For a simplified analysis, we held the thickness of the bottom liquid layer fixed, which resulted in the curvature and its derivate being expressed as:

$$\Delta^2 G = \frac{\partial^2 \Delta G}{\partial h_2^2} = \frac{A_{gs} - A_{s2} - A_{g1}}{2\pi h_2^4} + \frac{A_{g1}}{2\pi(h_2 - h_1)^4} - \left(\frac{S_{21}^{s,r}}{l^2}\right) \exp\left(\frac{d_0 - (h_2 - h_1)}{l}\right) \quad (5.7)$$

$$\Delta^3 G = \frac{\partial^3 \Delta G}{\partial h_2^3} = -2 \left(\frac{A_{gs} - A_{s2} - A_{g1}}{\pi h_2^5} \right) - \frac{2A_{g1}}{\pi(h_2 - h_1)^5} + \left(\frac{S_{21}^{s,r}}{l^3}\right) \exp\left(\frac{d_0 - (h_2 - h_1)}{l}\right) \quad (5.8)$$

The analysis for evaluating the bi-layer transition thickness h_T^{Bi} in a manner analogous to the single-layer case was performed for AgCo(5 nm) as shown in Fig. 5.3(c) and for CoAg(5 nm) as shown in Fig. 5.3(d). In addition, the $\Delta^2 G$ and $\Delta^3 G$ for varying bottom Co layer thickness (of 5, 7 and 10 nm) was compared for the AgCo system, as shown in Fig. 5.4.

Table 5.2: Magnitudes of the various parameters used in estimating the free energy and its derivatives for the bi-layer and single-layer system.

Parameter	Ag/Co/SiO ₂	Co/Ag/SiO ₂	Co/SiO ₂
A_{s2}	-9.19×10^{-19}	6.07×10^{-19}	$A: -3.1 \times 10^{-19}$
A_{gs}	-3.95×10^{-18}	-5.23×10^{-19}	$h_c: 0.293 \text{ nm}$
A_{g1}	1.01×10^{-19}	-1.04×10^{-19}	$\gamma: 1.882$
$S_{1s2}^{s,r}$	-2.07	1.4107	$S^p: 2.26$
$S_{21}^{s,r}$	-2.43	-2.32	$\theta: 101$
l_0	0.158nm	0.328nm	0.458nm

5.3.2.3 AgCo morphology behavior

Fig. 5.3(a) and (c) show the phase diagram of AgCo bi-layer system and free energy curvature for the AgCo(5 nm) system, respectively. We discuss a typical scenario, represented by the dashed vertical line (with ending arrow) drawn on Fig. 5.3(a) at a bottom layer thickness $h_1 = h_{Co} = 5 \text{ nm}$. This represents a general case where the top Ag layer thickness of the bi-layer system is varied with a constant Co bottom layer of 5 nm. As shown on the phase diagram, this line passes through various morphology regions, denoted by (a), (b) and (c), as well as various morphology transition points, represented by the roman numerals (I) and (II). The two most important results here are that, (1) the bi-layer system can have multiple morphology transitions, as evidenced at the points I and II, and (2) the morphology at lower thickness can be holes and then change to a bicontinuous state. Both of these features are absent in the single-layer, as seen in Fig. 5.1(c).

The corresponding locations of the regions and points are also indicated on the free energy curvature plot in Fig. 5.3(c). The immediate result apparent from Fig. 5.3(c) is that there is only a single minima in the curvature (as quantitatively evidenced from Fig. 5.4). This means that the bi-layer curvature can at most predict only one transition based on the curvature argument, and indeed, the minima corresponds to the first transition at point I. Therefore, the curvature-dependent approach in the bi-layer case is only partially able

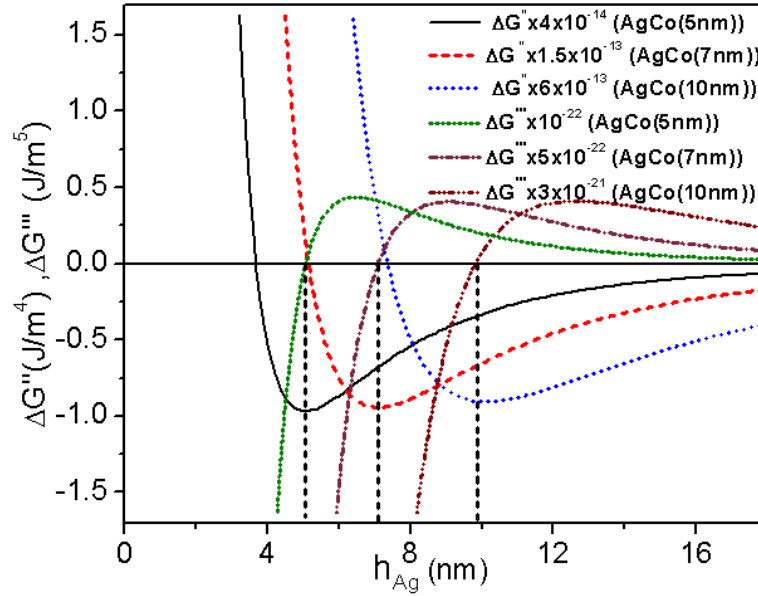


Figure 5.4: The second ($\Delta^2 G$) and third derivative ($\Delta^3 G$) of the free energy for the AgCo bi-layer system for varying values of the bottom Co layer thickness of 5, 7, and 10 nm calculated from Eq. 5.7 and Eq. 5.8. The minima in the $\Delta^2 G$ for each cases corresponds to the zero in the $\Delta^3 G$ (shown by the vertical dashed line for each case). The location of the zero in $\Delta^3 G$ represents the location of the first transition point in the bi-layer dewetting morphology.

to predict morphology transitions. The conclusion that can be drawn from this analysis is that the bi-layer AgCo phase diagram cannot be constructed from a knowledge of the bi-layer free energy. On the other hand, as Fig. 5.3(a) shows, it is possible to easily construct the diagram provided one knows the locations of the single-layer transitions for Ag and Co.

5.3.2.4 CoAg morphology behavior

Fig. 5.3(b) and (d) show the phase diagram of CoAg bi-layer system and free energy curvature of CoAg(5 nm) system, respectively. As for the AgCo case, a typical scenario is represented by the dashed line drawn at bottom layer thickness $h_1 = h_{Ag} = 5$ nm and vertical to the h_2 axis in Fig. 5.3(b). This represents the case where the top Co layer thickness of the bi-layer system is varied with a constant Ag bottom layer of 5 nm. Once again, on the phase diagram, this line passes through various morphology regions, denoted by (a), (b) and (c), as well as a morphology transition point marked as I. The intersection of regions a & b is a pseudo-transition while b & c corresponds to a phase transition. This bi-layer system has a single transition, and the morphology at lower thickness is the bicontinuous state and changes to holes, analogous to the single-layer system, as seen in Fig. 5.1(c). The corresponding locations of the regions and point are shown in Fig. 5.3(d). Again only one minima is evident and this corresponds to the location of the transition point marked on the phase diagram. Unlike the AgCo case described in Fig. 5.3(c), the transition now is from bicontinuous to holes, and this shows the additional uncertainty in utilizing the bi-layer free energy curvature in generalizing

the morphology on either side of the transition, in contrast to the single-layer system. Once again, we can conclude that the CoAg bi-layer curvature cannot predict the phase diagram. However, just as in the case of the AgCo system, as Fig. 5.3(b) shows, it is possible to easily construct the diagram provided the two single-layer transition points are known.

In this chapter we generated a free energy phase diagram which correlated with transition points in morphology as a function of the bilayer film thickness and arrangement.

Chapter 6

Formation of organized nanostructures from unstable bilayers of thin metallic liquids

(Reported to Physics of Fluids, vol 23, 122105(2011))

6.1 Summary

Dewetting of pulsed-laser irradiated, thin (< 20 nm), optically reflective metallic bilayers on an optically transparent substrate with a reflective support layer is studied within the lubrication equations model. A steady state bilayer film thickness (h) dependent temperature profile is derived based on the mean substrate temperature estimated from the elaborate thermal model of transient heating and melting/freezing. Large thermocapillary forces are observed along the plane of the liquid-liquid and substrate-liquid interfaces due to this h -dependent temperature, which, in turn, is a consequence of the h -dependent laser light reflection and absorption. Consequently the dewetting is a result of the competition between thermocapillary and intermolecular forces. A linear analysis of the dewetting length scales established that the non-isothermal calculations better predict the experimental results as compared to the isothermal case within the bounding Hamaker coefficients. Subsequently, a non-linear dynamics study of the dewetting pathway was performed for Ag/CO and Co/Ag bilayer systems to establish the morphology of during the dewetting pathway. We found that the system evolves via formation of different morphologies, including core-shell, embedded, or stacked nanostructure morphologies.

6.2 Problem statement

6.2.1 Evolution equations for the bilayer

We consider a bilayer thin film, which is comprised of two superposed layers of immiscible Newtonian liquids, for instance the molten Co and Ag; see Fig. 6.1.

The lower layer rests on a solid, planar substrate (denoted by the subscript s hereafter) that has thickness h_s , and the upper layer is in contact with the adjacent gas phase. The locations of the liquid-liquid and the liquid-gas interfaces are given by $z = h_1(x, t)$ and $z = h_2(x, t)$, respectively, where z, x are the vertical and the horizontal coordinates, respectively, with $z = 0$ corresponding to the location of substrate/liquid interface. The bilayer is irradiated by a single pulsed laser beam, such that the pulse width typically is 10 ns, and the frequency of pulses is 50 Hz.

In the case of a single-layer film, dewetting has been successfully modeled as continuous in time by treating the film as liquid despite that it re-solidifies after each pulse. Thermocapillary effect owing to latent heat release is negligible due to extremely large cooling rates involved [37]; the film cools down so fast that there is insufficient time for any morphology change [62], and the next incident laser pulse effectively quenches in the film. The time and length scales involved and the resulting morphologies are captured very well by such models [175, 37, 49].

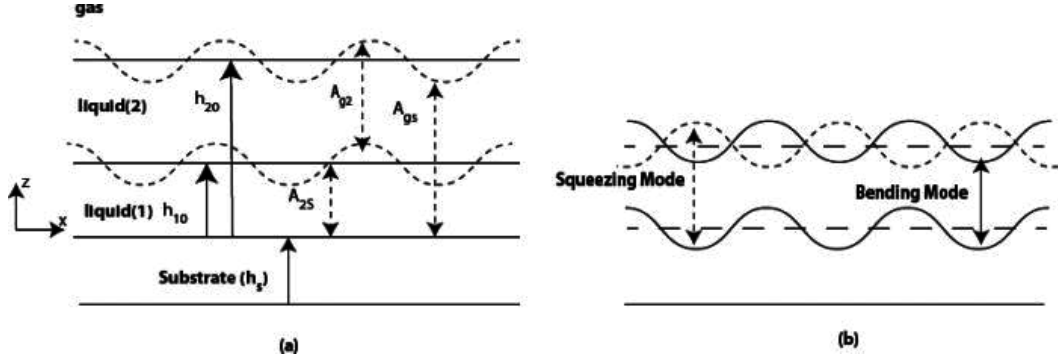


Figure 6.1: (a) Liquid bilayer/substrate system. Here A_{g2} , A_{gs} and A_{2s} are Hamaker coefficients of the intermolecular repulsion or attraction force, h_{10} , h_{20} are the unperturbed thicknesses of the liquid layers, and h_s is the thickness of SiO_2 substrate. Si support layer is not shown. (b) Deformation modes of the two interfaces.

In this paper we adopt the same strategy for the bilayer film modeling. Hereafter, a two-dimensional geometry is considered; thus we assume that liquid flow is negligible in the transverse direction.

The derivation of the evolution equations for the functions $h_{1,2}(x,t)$, describing the shapes of the two interfaces, is detailed in Ref. [167] in the isothermal case, and in Refs. [166, 171, 172] in the more general non-isothermal case characterized by the presence of thermocapillary (Marangoni) forces. (Hereafter, the notation $f_{\alpha,\beta}$ means f_α, f_β .) These derivations assume that the characteristic spatial scale in the x -direction is much larger than in the z -direction (layers are thin), so that the fluid flow in the layers is described by Stokes equations. The derivation procedure is routinely called the long-wave (or lubrication) approximation. A thorough discussions of the long-wave approach to the studies of the instabilities of thin liquid films can be found in the review papers [215, 216, 217].

Here we start with the non-isothermal system of equations, where the thermocapillary effect is accounted for at the liquid-liquid and liquid-gas interfaces [165, 166, 171, 172]:

$$\partial_t h_1 = -\partial_x [F_{11} \partial_x P_1 + F_{12} \partial_x P_2 + \Phi_{11} \partial_x \sigma_1 + \Phi_{12} \partial_x \sigma_2], \quad (6.1)$$

$$\partial_t h_2 = -\partial_x [F_{21} \partial_x P_1 + F_{22} \partial_x P_2 + \Phi_{21} \partial_x \sigma_1 + \Phi_{22} \partial_x \sigma_2], \quad (6.2)$$

where $P_{1,2}$ are the pressures and $\sigma_{1,2}$ are the surface tensions of the liquid-liquid and liquid-gas interface, respectively. The quantities F_{ij} and Φ_{ij} , $i, j = 1, \dots, 2$ are given by:

$$F_{11} = -\frac{1}{3\eta_1} h_1^3, \quad F_{12} = -\frac{1}{2\eta_1} h_1^2 \left(h_2 - \frac{h_1}{3} \right), \quad (6.3)$$

$$F_{21} = \frac{1}{6\eta_1} h_1^3 - \frac{1}{2\eta_1} h_1^2 h_2, \quad F_{22} = \frac{1}{3} (h_2 - h_1)^3 \left(\frac{1}{\eta_1} - \frac{1}{\eta_2} \right) - \frac{1}{3\eta_1} h_2^3, \quad (6.4)$$

$$\Phi_{11} = \Phi_{12} = \frac{1}{2\eta_1} h_1^2, \quad \Phi_{21} = -\frac{1}{2\eta_1} h_1 (h_1 - 2h_2), \quad (6.5)$$

$$\Phi_{22} = \frac{1}{2\eta_2} (h_2 - h_1)^2 + \Phi_{21}, \quad (6.6)$$

where $\eta_{1,2}$ are the dynamic viscosities. The pressures are:

$$P_1 = -\sigma_1 \partial_{xx} h_1 - \sigma_2 \partial_{xx} h_2 + \Pi_1(h_1, h_2) + \rho_1 g h_1 + \rho_2 g (h_2 - h_1), \quad (6.7)$$

$$P_2 = -\sigma_2 \partial_{xx} h_2 + \Pi_2(h_1, h_2) + \rho_2 g h_2, \quad (6.8)$$

where $\rho_{1,2}$ are the densities, g is the acceleration of gravity, and $\Pi_{1,2}(h_1, h_2)$ are the disjoining pressures, given by

$$\Pi_1(h_1, h_2) = \frac{A_{2s}}{h_1^3} + \frac{A_{gs}}{h_2^3} + \frac{S_1 \exp\left(-\frac{h_1}{\ell_1}\right)}{l_1}, \quad (6.9)$$

$$\Pi_2(h_1, h_2) = \frac{A_{g2}}{(h_2 - h_1)^3} + \frac{A_{gs}}{h_2^3} + \frac{S_2 \exp\left(-\frac{(h_2 - h_1)}{\ell_2}\right)}{l_2}. \quad (6.10)$$

Here, A_{g2}, A_{gs}, A_{2s} are the Hamaker coefficients describing the *long-range molecular repulsion or attraction*, depending on the sign of a coefficient (see Table II), between the liquid-liquid and liquid-gas interface, solid-liquid and liquid-gas interface, and solid-liquid and liquid-liquid interface, respectively. $S_{1,2} < 0$ are the spreading coefficients, describing the *short-range molecular repulsion* between the solid-liquid and liquid-liquid interface, and liquid-liquid and liquid-gas interface, respectively. $\ell_{1,2}$ are the equilibrium cut-off distances. The short-range repulsion between the solid-liquid and liquid-gas interface is not included. Note that we include gravity terms in the pressures, since it has been shown that these terms may be important in a certain range of parameters [168, 173].

The surface tension gradients, $\partial_x \sigma_1$ and $\partial_x \sigma_2$, are caused by the gradients of the temperature at the liquid-liquid and the liquid-gas interface, respectively. We assume linear dependence of the surface tensions on temperature:

$$\sigma_1 = \sigma_1^{(m)} - \gamma_1 \left(T_1(z = h_1) - T_1^{(m)} \right), \quad \gamma_1 > 0, \quad T_1(z = h_1) > T_1^{(m)}, \quad (6.11)$$

$$\sigma_2 = \sigma_2^{(m)} - \gamma_2 \left(T_2(z = h_2) - T_2^{(m)} \right), \quad \gamma_2 > 0, \quad T_2(z = h_2) > T_2^{(m)}, \quad (6.12)$$

where $\sigma_{1,2}^{(m)}$ are the surface tensions at the corresponding melting temperatures $T_{1,2}^{(m)}$. Since the temperatures $T_{1,2}$ will be shown to depend on the thicknesses of the layers, the surface tension gradients in Eqs. (6.1), (6.2) are written as

$$\partial_x \sigma_1 = -\gamma_1 \left((\partial_{h_1} T_1)|_{z=h_1} \partial_x h_1 + (\partial_{h_2} T_1)|_{z=h_1} \partial_x h_2 \right), \quad (6.13)$$

$$\partial_x \sigma_2 = -\gamma_2 \left((\partial_{h_1} T_2)|_{z=h_2} \partial_x h_1 + (\partial_{h_2} T_2)|_{z=h_2} \partial_x h_2 \right). \quad (6.14)$$

Note that in the presented formulation, the surface tensions $\sigma_{1,2}$ in the pressures (6.7) and (6.8) are treated as constants (which have the numerical values given by Eqs. (6.11), (6.12), where the temperatures are evaluated at $h_{10,20}$), i.e. the mentioned surface tension gradient, or thermocapillary, terms contain all information on the effects of the surface tensions changes along the interfaces.

In order to close the equation set, we need the specification of the thermal problem. This is discussed in

the next section.

6.2.2 Thermal problem

The steady-state, long-wave energy equations in the two metallic layers and in the thin, purely conductive substrate are [175, 37]

$$\frac{\kappa_{1,2}}{\rho_{1,2}C_{eff}}\partial_{zz}T_{1,2} + \frac{\delta_2 J}{\rho_{1,2}C_{eff}}(1 - R(h_1, h_2 - h_1))\exp(\delta_{1,2}(z - h_2)) = 0, \quad (6.15)$$

$$\frac{\kappa_s}{\rho_s C_{eff}}\partial_{zz}T_s = 0, \quad (6.16)$$

where $\kappa_{1,2,s}$ are the thermal conductivities, C_{eff} is the effective heat capacity, $\delta_{1,2}$ are the optical absorption coefficients, $\delta_2 J$ is the rate of the laser energy flux volumetric absorption into the upper layer, ρ_s is the substrate density, and $R(h_1, h_2 - h_1)$ is the dimensionless effective reflectivity function, which has been calculated using the method described in detail in Ref. [218]. Eq. (6.15) is the Beer-Lambert law for the bilayer.

Fig. 6.2(a) shows the contour plot of the reflectivity for Ag/Co/SiO₂/Si system. It can be seen that the reflectivity is shaped, roughly, like a Taco shell with the axis that makes the 120 degrees angle to the horizontal axis in the plot. The plot for Co/Ag/SiO₂/Si system is similar. Fig. 6.2(b) shows the reflectivity of the Ag/Co/SiO₂/Si and Co/Ag/SiO₂/Si as a function of a varying thickness of the top film, with the thickness of the bottom film fixed at 1 nm. The thickness of the SiO₂ substrate is taken as 400 nm, consistent with the experimental system [42] to which we will compare our calculations. The non-monotonic dependence of the reflectivity on thickness is clearly evident from either plot, as is the increase of reflectivity as the thickness of the top film approaches zero. This is the result of increased reflectivity from the underlying reflective Si layer. This thickness dependent absorption (Eq. 6.15) and reflectivity are responsible for the thermocapillary forces that arise along the interfaces of the liquid-ambient and liquid-liquid interfaces.

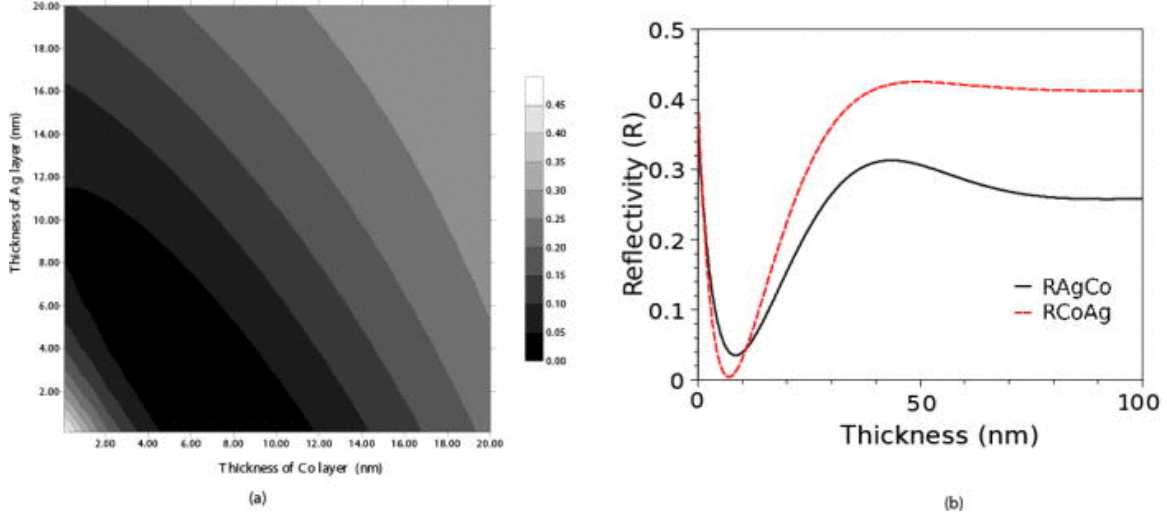


Figure 6.2: (Color online). (a) Contour plot of the reflectivity for Ag/Co/SiO₂/Si system. The increased reflectivity when approaching zero top film thickness is due to the reflective underlying Si layer. (b) Reflectivity R of the bilayer metallic systems Ag/Co/SiO₂/Si and Co/Ag/SiO₂/Si as a function of a varying thickness of the top film; thickness of the bottom film is 1 nm.

The long-wave boundary conditions for the set (6.15), (6.16) are

$$z = h_2 : \quad \kappa_2 \partial_z T_2 = -\alpha (T_2 - \Theta_a), \quad (6.17)$$

$$z = h_1 : \quad \kappa_1 \partial_z T_1 = \kappa_2 \partial_z T_2, \quad T_1 = T_2, \quad (6.18)$$

$$z = 0 : \quad \kappa_1 \partial_z T_1 = \kappa_s \partial_z T_s, \quad T_1 = T_s, \quad (6.19)$$

$$z = -h_s : \quad T_s = \Theta_s, \quad (6.20)$$

where Θ_a and Θ_s are the (constant) gas and substrate temperatures, respectively, and α is the heat transfer coefficient at the liquid-gas interface.

The solution of this boundary-value problem in the liquid layers has the form

$$T_1 = -\frac{\delta_2 J (1 - R(h_1, h_2 - h_1))}{\delta_1^2 \kappa_1} \exp(\delta_1 (z - h_2)) + c_{11} z + c_{12}, \quad (6.21)$$

$$T_2 = -\frac{J (1 - R(h_1, h_2 - h_1))}{\delta_2 \kappa_2} \exp(\delta_2 (z - h_2)) + c_{21} z + c_{22}, \quad (6.22)$$

where c_{ij} are the complicated functions of $h_{1,2,s}$, $\kappa_{1,2,s}$, $\delta_{1,2}$, J , α , Θ_a , Θ_s , which we obtained using the computer algebra system (CAS) (Mathematica). (In the substrate, the temperature is an increasing linear function of z , as is evident from Eq. (6.16). In contrast to bilayer films heated from the substrate [172], the temperature profile (6.21), (6.22) is nonlinear in z ; it formally reverts to a linear one when $R = 1$.)

In the above presented formulation the heat conduction in the thick Si support layer is disregarded, and the temperature at the SiO₂/Si interface is set equal to the mean substrate temperature Θ_s , estimated from the transient heating model for the typical values of the laser energy and the bilayer film thickness employed

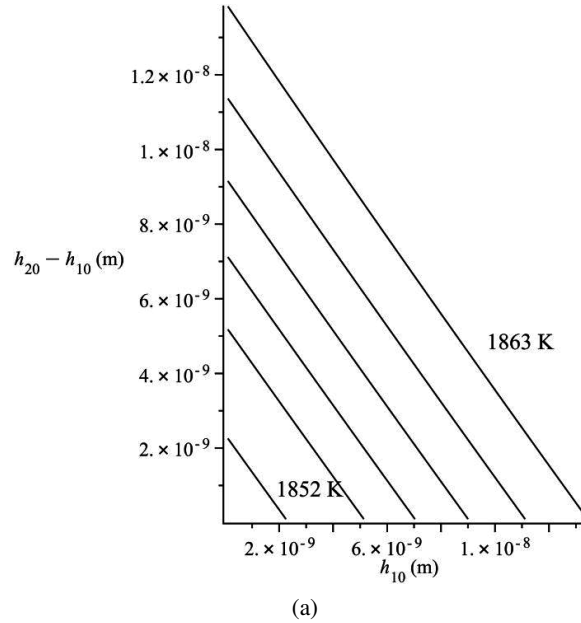


Figure 6.3: Typical contour plot of the interface temperature as a function of h_1 and h_2 .

in this study (see Appendix). Θ_s is obtained by averaging over many pulses the temperature rise and fall within the width of the Gaussian pulse. The formulation of the boundary conditions (6.17)-(6.20) that makes use of the mean temperature is the only one possible within the context of the standard lubrication model, where the temperature distribution is steady-state and thus its determination requires knowledge of the mean temperature. Practically, this formulation also makes feasible the numerical evaluation, at every step of interface evolution, of the complicated analytical solution formulas for the steady-state temperatures of the metal layers and for the derivatives of these temperatures with respect to thicknesses h_1 and h_2 . Note also, that even without accounting for the heat conduction in the support layer, this layer still exerts the important influence on the system's steady-state temperature field, since the effective reflectivity R is calculated for the full system metal₁/metal₂/SiO₂/Si.

Ignoring the transient nature of heat conduction due to intermittency of pulses is justified if the thermal diffusion time scale τ_H is much shorter than the dewetting time scale τ_D . In our previous works on single-layer films we have shown that $\tau_H \sim h^4$, and $\tau_D \sim h^5$. Thus for sufficiently thick films $\tau_H < \tau_D$. In the bilayer system we expect similar general trend.

Fig. 6.3 shows the contour plot of either interface temperature, $T_1(z = h_1)$ or $T_2(z = h_2)$; in the case of the latter figure, the plotting program can't resolve the small difference (less than 1 K) of the interface temperatures. From Fig. 6.3(a) one observes that the temperature is nearly uniform across the bilayer (*however*, the derivatives with respect to the thickness are not necessarily uniform). Note also from both figures that the temperature difference between the liquid/gas interface and the SiO₂/Si interface is small (of the order of 15 K or less). This parallels the results of the analysis of the model of transient heating, see Appendix and Ref. [37]

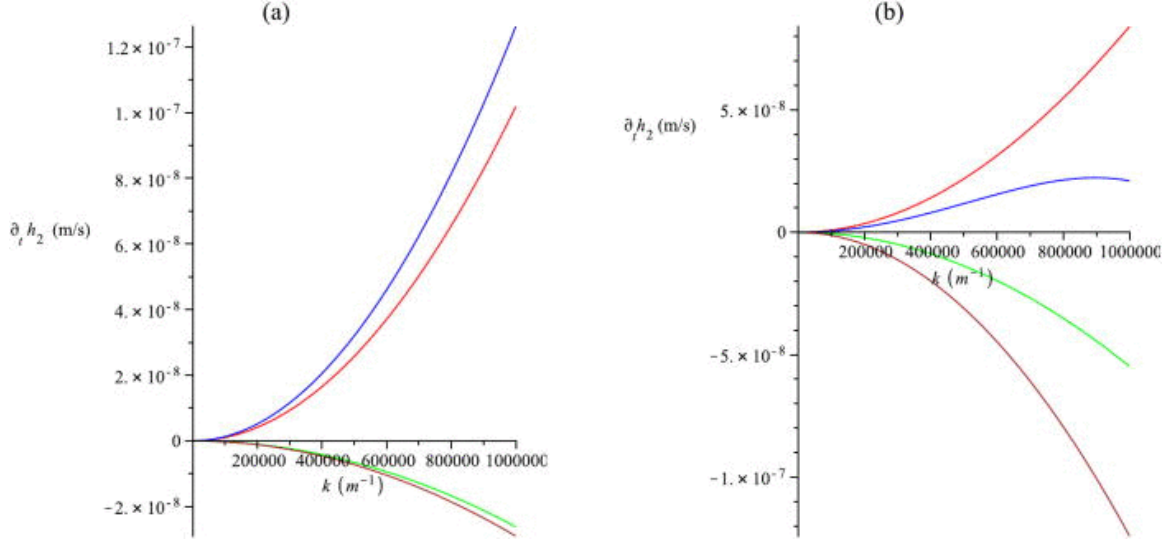


Figure 6.4: (Color online). The linearized terms at the RHS of Eq. (6.2) at the interfacial deformations with the amplitude 0.1 nm from the mean values (a) $h_{10} = 5$ nm, $h_{20} = 7$ nm, (b) $h_{10} = 5$ nm, $h_{20} = 17$ nm. Red line: 1st term; blue line: 2nd term; green line: 3rd term; brown line: 4th term. Values along the vertical axis show the *contribution* of each term to the total velocity of the interface, not the total velocity itself.

Next we show that despite the typical temperature difference being small, the contributions from the thermocapillary surface tension gradient terms in the evolution equations (6.1) and (6.2) are significant. Indeed, for Ag/Co/SiO₂/Si system, Fig. 6.4 shows the comparison of the linearized terms at the RHS of the evolution equation (6.2). These terms are calculated at the amplitudes of the interfaces deformations that are set equal to 0.1 nm, the values that are within reach of the linear approximation, see Fig. 6.10 in the Section 5.2.2. (Deformation = amplitude $\times$ $\cos kx$, see Section 5.2.2 for more details on the linear stability analysis.) It can be seen that for *thin* films - that are the sole focus of this paper - the thermocapillary surface tension gradient terms 3 and 4 are negative and thus stabilizing, and their magnitudes are of the same order as the magnitudes of the pressure gradient terms 1 and 2. Same can be said of the terms at the RHS of the first evolution equation (6.1). Terms 3 and 4 are also negative for the parameters of the Co/Ag/SiO₂/Si system. For *thick* films ($h_{20} > 32$ nm for Ag/Co), these terms become positive and thus *destabilizing*. Thus the situation here is similar to the case of a single-layer film; in Ref. [37] it is shown that Co films on the SiO₂ substrate are destabilized by the thermocapillary forces at thicknesses larger than roughly 10 nm. For bilayers of Ag/Co on SiO₂/Si this threshold value is larger, possibly due to the reflectivity of the Si, which results in the distinctly different reflectivity curve of the system for small thicknesses.

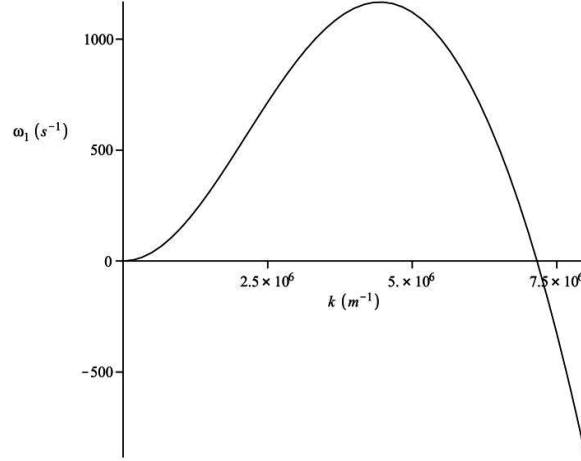


Figure 6.5: Typical positive dispersion curve for the Ag/Co/SiO₂/Si system.

Destabilization by thermocapillarity in thick Ag/Co films is manifested in the appearance of the secondary maximum on the linear dispersion curve at small wavenumbers. With the increase of h_{20} , this maximum grows fast and soon the associated wavelength prevails. We call this effect the *exchange of stability*. Thus this kind of destabilization leads to a larger spacing between particles upon dewetting. In Co/Ag films, the exchange of stability emerges in thin films (see Fig. 6.7), but the nature of the exchange is connected to the change of the energetics of the intermolecular forces as thickness changes, and not to the thermocapillary destabilization. That is, thermocapillarity stabilizes thin Co/Ag films, just as it does stabilize thin Ag/Co films, as has been discussed.

6.2.3 Parameters

The typical values of the physical parameters for the Ag/Co/SiO₂/Si and Co/Ag/SiO₂/Si systems are shown in the Table I. Also, in the Table II we show the signs of the Hamaker coefficients for the various pairs of interfaces in Fig 6.1. To the best of our knowledge, the *magnitudes* of the Hamaker coefficients for the metallic systems like Ag/Co/SiO₂/Si or Co/Ag/SiO₂/Si are not known with precision and vary based on the type of calculation used to evaluate them, as noted in [42]. Generally, values of the Hamaker coefficients may vary from 10^{-22} J to 10^{-18} J [219, 177]. The choice of values of the Hamaker coefficients is very important, as has been emphasized in the published studies of thin bilayer systems [166, 167, 168]. Here we have utilized the two sets of coefficients used in [42] which successfully bounded the experimental values based on the energy rate theory. Here the two sets were utilized for the isothermal and non-isothermal linear stability analysis theoretical predictions of the experimental and their magnitudes. The results of the calculation of the spacing are show in Figs. 6.6 and 6.8 for the Ag/Co and Co/Ag systems respectively. In each figure, there are two pairs of trends. One pair corresponds to two sets of coefficients in isothermal calculations, and the other corresponds to the non-isothermal calculation. The bounds provided by the non-isothermal pair are shown by the striped region. From both figures it is evident that the non-isothermal values provide better overall predictions to the experimental measurements.

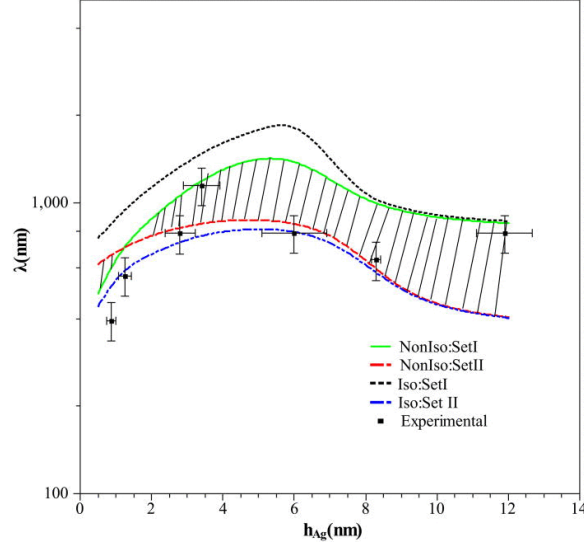


Figure 6.6: Particle spacing vs. the thickness of the top layer, for Ag/Co/SiO₂/Si system with the Co layer thickness fixed at 5 nm. Closed squares correspond to the experimentally determined particle spacings [42]. The solid (green) and dashed (red) lines enclosing the striped region correspond to the non-isothermal calculations, with the solid line corresponding to coefficient set I, and dashed line corresponding to coefficient set II (Table 6.2). The short-dash (black) and dash-dotted (blue) lines correspond to the isothermal calculations with the top line for set I and bottom for set II.

It must be noted here that bilayer dynamics is very rich even in the isothermal case and can exhibit a large variety of evolution modes and outcomes, as was first noted by Pototsky *et al* [165]. Bandyopadhyay, Gulabani, & Sharma [167] built a classification scheme of all possible evolution modes for the general isothermal polymer bilayer system, based on the extensive linear stability analysis supported by some non-linear simulations. Our work extends this existing bilayer work by incorporating thermocapillary effects in the linear and nonlinear analysis for metallic liquids. For purposes of comparison, the two bilayer systems we have investigated can be most closely compared to Bandopadhyay *et al* work via the surface energy classification scheme they have used. For example, the Co/Ag/SiO₂/Si system investigated here is similar to the case 3 in Bandopadhyay *et al* as the surface energies of the substrate/gas interface ($\sigma_{sg} = 0.025 \text{ J/m}^2$), liquid₁ (Ag)/gas interface ($\sigma_{1g} = 0.925 \text{ J/m}^2$), and liquid₂ (Co)/gas interface ($\sigma_{2g} = 1.88 \text{ J/m}^2$) are related as $\sigma_{sg} < \sigma_{1g} < \sigma_{2g}$, while the Ag/Co/SiO₂/Si system is similar to their case 4, since $\sigma_{sg} < \sigma_{2g} < \sigma_{1g}$.

For convenience and ease of comparison with the results of the experiments we keep equations in the dimensional form. Another reason for working with the dimensional equations is that it is simply difficult to find convenient scales for the non-isothermal bilayer system (see Refs. [166, 168, 171, 175]) and, no matter how the scales are chosen, due to the large number of physical parameters (27 total, including the parameters in Tables I and II), the number of dimensionless parameters will still be very large. In this paper, since the material system is fixed from the outset, we study the impacts of four parameters only: the upper

Table 6.1: The physical parameters.

Ag/Co/SiO ₂ /Si system	Co/Ag/SiO ₂ /Si system
$\eta_1 = 4.46 \times 10^{-3}$ Pa-s	$\eta_1 = 3.88 \times 10^{-3}$ Pa-s
$\eta_2 = 3.88 \times 10^{-3}$ Pa-s	$\eta_2 = 4.46 \times 10^{-3}$ Pa-s
$\sigma_1^{(m)} = 0.168$ J/m ²	$\sigma_1^{(m)} = 0.168$ J/m ²
$\sigma_2^{(m)} = 0.925$ J/m ²	$\sigma_2^{(m)} = 1.88$ J/m ²
$\gamma_1 = \gamma_2 = 5 \times 10^{-5}$ J/(K m ²)	$\gamma_1 = \gamma_2 = 5 \times 10^{-5}$ J/(K m ²)
$\rho_1 = 7.75 \times 10^3$ Kg/m ³	$\rho_1 = 9.32 \times 10^3$ Kg/m ³
$\rho_2 = 9.32 \times 10^3$ Kg/m ³	$\rho_2 = 7.75 \times 10^3$ Kg/m ³
$T_1^{(m)} = 1768$ K	$T_1^{(m)} = 1235$ K
$T_2^{(m)} = 1235$ K	$T_2^{(m)} = 1768$ K
$\Theta_a = 300$ K	$\Theta_a = 300$ K
$\Theta_s = 1850$ K	$\Theta_s = 1850$ K
$\delta_1 = \delta_2 = 10^6$ m ⁻¹	$\delta_1 = \delta_2 = 10^6$ m ⁻¹
$\alpha = 10^3$ W/(K m ²)	$\alpha = 10^3$ W/(K m ²)
$\kappa_1 = 34$ W/(K m)	$\kappa_1 = 185$ W/(K m)
$\kappa_2 = 185$ W/(K m)	$\kappa_2 = 34$ W/(K m)
$\kappa_s = 50$ W/(K m)	$\kappa_s = 50$ W/(K m)
$h_s = 400$ nm	$h_s = 400$ nm
$J = 1.25 \times 10^{11}$ J/(s m ²)	$J = 1.25 \times 10^{11}$ J/(s m ²)

Table 6.2: Hamaker coefficients for the Ag/Co/SiO₂/Si system.

Hamaker const.	Set I	Set II
A_{g2}	$-10^{20}J$	$-10^{19}J$
A_{gs}	$4 \times 10^{20}J$	$4 \times 10^{20}J$
A_{2s}	$4 \times 10^{21}J$	$2 \times 10^{20}J$

Table 6.3: Hamaker coefficients for the Co/Ag/SiO₂/Si system.

Hamaker const.	Set I	Set II
A_{g2}	$10^{-20}J$	$10^{-21}J$
A_{gs}	$10^{20}J$	$10^{-18}J$
A_{2s}	$-10^{-22}J$	$-10^{-22}J$

layer thickness $h_{20} - h_{10}$ (where h_{10} is fixed), and the two sets of Hamaker coefficients.

6.3 Linear stability analysis

Problem (6.1) - (6.14), (6.21), (6.22) has a trivial, uniform equilibrium solution $h_1(x) = h_{10}$, $h_2(x) = h_{20}$. We introduce small perturbations $\xi_1(x, t) = U(t) \exp(ikx)$, $\xi_2(x, t) = V(t) \exp(ikx)$ (where k is the wavenumber, and $U(t)$, $V(t)$ are the time-dependent small amplitudes) through $h_{1,2}(x, t) = h_{10,20} + \xi_{1,2}(x, t)$, and substitute the latter forms into the system (6.1) - (6.14), (6.21), (6.22). Linearizing in $U(t), V(t)$ gives the linear ODE system

$$\dot{U}(t) = a_{11}U(t) + a_{12}V(t), \quad (6.23)$$

$$\dot{V}(t) = a_{21}U(t) + a_{22}V(t), \quad (6.24)$$

where the coefficients a_{ij} are the complicated functions (determined again with the help of the CAS) of $k, h_{10,20}$, the Hamaker coefficients, and other physical parameters. Next, substitution of $U(t) = u \exp(\omega t)$, $V(t) = v \exp(\omega t)$ into the system (6.23), (6.24) results in the linear, homogeneous algebraic system for u and v :

$$(a_{11} - \omega)u + a_{12}v = 0, \quad (6.25)$$

$$a_{21}u + (a_{22} - \omega)v = 0. \quad (6.26)$$

The condition for existence of a non-trivial solution to this system is when the determinant of the system's matrix equals zero, which translates into the quadratic equation for the linear growth rate ω :

$$\omega^2 - (a_{11} + a_{22})\omega + a_{11}a_{22} - a_{12}a_{21} = 0. \quad (6.27)$$

The latter equation may have two real and distinct solutions, one real solution, or two complex conjugate solutions. For the parameters of interest in this paper, only the first situation was ever found. In other words, only the monotonous modes of instability were detected.

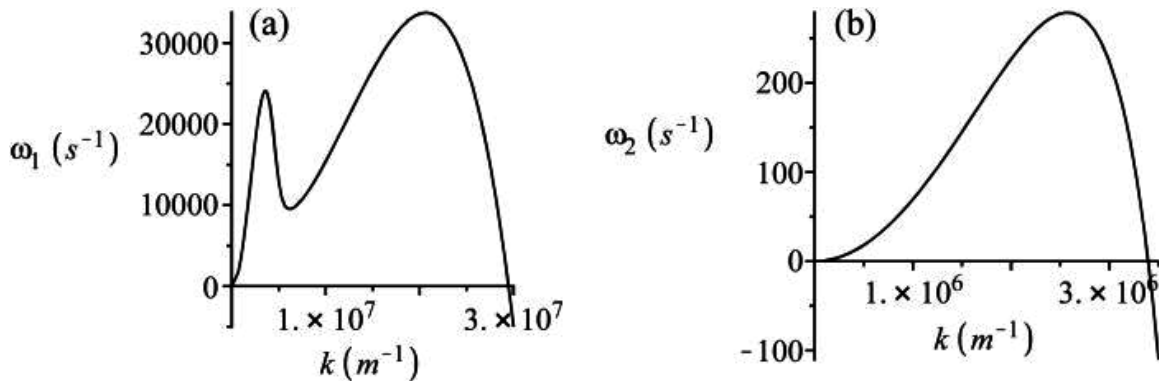


Figure 6.7: Typical positive dispersion curves for the Co/Ag/SiO₂/Si system. Both ω_1 and ω_2 occur simultaneously as the solutions of Eq. (6.27).

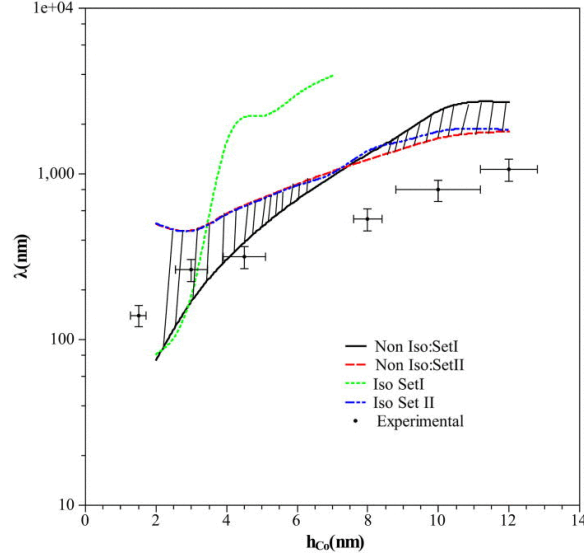


Figure 6.8: Particle spacing vs. the thickness of the top layer, for Co/Ag/SiO₂/Si system with the Ag layer thickness fixed at 5 nm. Closed squares correspond to the experimentally determined particle spacings [42]. The solid (black) and dashed (red) lines enclosing the striped region correspond to the non-isothermal calculations, with the solid line corresponding to coefficient set I, and dashed line corresponding to coefficient set II (Table 6.3). The short-dash (green) and dash-dotted (blue) lines correspond to the isothermal calculations with the top line for set I and bottom for set II.

6.3.1 Ag/Co/SiO₂/Si system

For the Ag/Co/SiO₂/Si system one solution of Eq. (6.27), $\omega_1(k)$, changes sign at a certain (single) value of k , and the second solution, $\omega_2(k)$ is negative for all k . The typical dependence of ω_1 on k is shown in Fig. 6.5. Such dependence, characterized by a single maximum, is typical of long-wave instabilities. The value of k which corresponds to the maximum point on the $\omega_1(k)$ curve is the most dangerous (or critical) wavenumber of instability. The corresponding wavelength, $\lambda = 2\pi/k_{max}$, can be observed in the experiment: it has been shown that λ is a quite accurate measure of the particle spacing in the dewetting experiments on thin metal films [59].

The theory prediction of the particle spacings vs. the thickness of the top (Ag) layer are shown in Fig. 6.6 for the two sets of the Hamaker coefficients, and compared to the experimentally determined particle spacings (closed squares). The experimentally determined values were taken from Ref. [42]. The bottom layer (Co) thickness was kept constant at 5 nm. In this Figure, the non-isothermal and isothermal predictions for each set of coefficients is shown, and the non-isothermal bounds are shown by the striped region. It can be seen that the non-isothermal calculation is a better overall predictor of the experimental data as compared to the isothermal case. In the simulations to be presented in Sec. IV we compare results from both sets of coefficients because, together they provide a better overall prediction over the entire range of film thickness studied.

In Ref. [167] the following criterion is suggested for the determination of the deformation mode type *in*

the linear (small interface deformation) regime: if the ratio

$$Q_L = \frac{\omega_{max} - a_{11}(k_{max})}{a_{12}(k_{max})} \quad (6.28)$$

is positive [see Eqs. (6.25), (6.26)], then the deformation mode is bending, otherwise it is squeezing (see Fig. 6.1). We applied this criterion to the Ag/Co/SiO₂/Si system *under isothermal and non-isothermal conditions*, and obtained the bending mode. This agrees fully with Ref. [167].

6.3.2 Co/Ag/SiO₂/Si system

For the Co/Ag/SiO₂/Si system both solutions of Eq. (6.27) can change a sign at a certain (single) value of k (two-mode instability). However, the magnitude of the second solution, $\omega_2(k)$, is much less than the magnitude of the first solution, and thus the critical wavelength is still determined by the first solution. The typical dependencies of ω_1 and ω_2 on k are shown in Fig. 6.7. Note that the graph of ω_1 has both the relative and the absolute maxima; the critical wavenumber is one that corresponds to the absolute maximum. As the thickness of the top layer increases, the critical wavenumber approaches zero fast (thus λ increases), the more so if the exchange of stability occurs, in which case the critical wavenumber experiences a jump. For the upper layer thickness larger than 11 nm both solutions become negative. Thus thick bilayers are linearly stable.

The graphs of the particle spacings vs. the thickness of the top (Co) layer are shown in Fig. 6.8 for the two sets of the Hamaker coefficients, and compared to the experimentally determined particle spacings (closed squares). The bottom layer (Ag) thickness was kept constant at 5 nm. As in Figure 6.6, the non-isothermal and isothermal predictions for the two sets are shown, with the non-isothermal case emphasized by the striped pattern. Again, it can be seen that the non-isothermal calculation is a better overall predictor of the experimental data. One feature seen with the first set of the Hamaker coefficients is the abrupt jump in λ from 184 nm to 1550 nm when h_{Co} changes from 3 nm to 4 nm. This is due to the exchange of stability, signaling nearly the ten-fold decrease of the critical wavenumber. On the other hand, in the non-isothermal case the second maximum is always larger than the first one and no such abrupt growth of the wavelength occurs. Similar jump in λ , but of much smaller magnitude, occurs in the isothermal case also for the second set of the Hamaker coefficients.

The application of the criterion (6.28) to the isothermal and non-isothermal Co/Ag/SiO₂/Si system indicates the squeezing mode of evolution (*in the linear regime*) for the first set of the Hamaker coefficients, and the bending mode for the second set.

6.4 Computations of the bilayer dewetting and morphology evolution

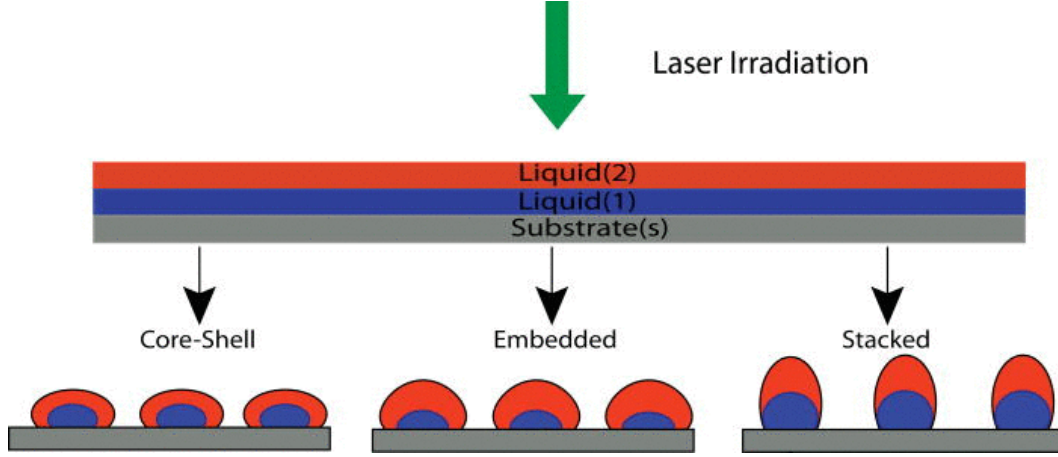


Figure 6.9: Sketch of the different self-organized nanostructure morphologies that can result from bilayer dewetting.

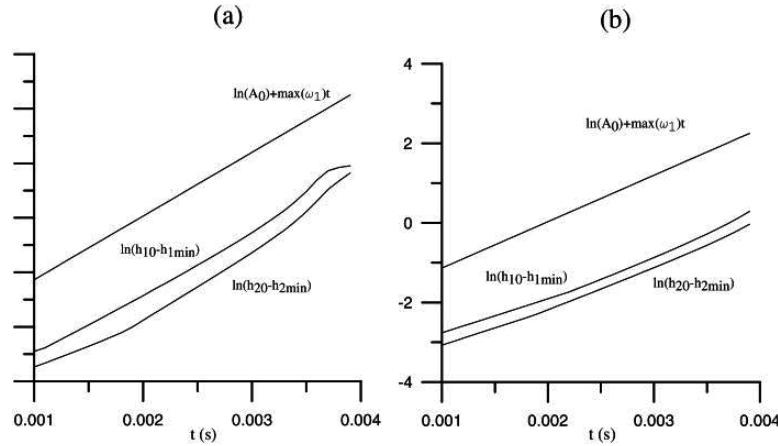


Figure 6.10: Comparison of the computed growth rate of instability to the one predicted by the linear theory (Ag/Co, coefficient set I, see Fig. 6.11 for the film profiles). (a) Spatial grid resolution is 200 points; (b) 400 points. h_{1min} and h_{2min} are the minimum thicknesses of the layers over the computational domain.

Evolution equations (6.1), (6.2) were solved numerically using the method of lines. Integration in time is performed using the stiff ODE solvers RADAU or DVODE, whereas the discretization in space is carried out in the conservative form using the second order finite differencing with half-node interpolation, on a spatially uniform grid. Below we describe the results of the computations in the non-isothermal regime and compare, where appropriate, to the corresponding “isothermal” results. Dynamics of both systems was computed with the two sets of the Hamaker coefficients that are shown in the captions to Figs. 6.6 and 6.8. For the Ag/Co/SiO₂/Si system the outcomes are very similar, thus in the next section we present the results only for the first set of coefficients. For the Co/Ag/SiO₂/Si system the outcomes are quite different, thus we

discuss the results for both sets of coefficients. Each run tracks the evolution of the most dangerous mode, λ , from the linear stability analysis. The length L of the computational domain in the x -direction equals 4λ . Periodic boundary conditions are imposed at $x = 0$ and $x = L$. The initial condition is small, uncorrelated, volume-preserving random perturbations of the mean thicknesses $h_{10,20}$ of the layers. To avoid films rupture at the substrate and to get insight into the dynamics of coarsening, the spreading coefficients were set to non-zero negative values $S_1 = -0.9 \text{ J/m}^2$, $S_2 = -0.3 \text{ J/m}^2$ (unless otherwise noted); the cut-off lengths are $\ell_{1,2} = 0.2 \text{ nm}$. During each run, we also monitor the integral measure suggested by Pototsky *et al* [166],

$$Q_{NL} = \frac{1}{L} \int \frac{(h_1 - h_{10})(h_2 - h_{20})}{[(h_1 - h_{10})^2 + (h_2 - h_{20})^2]} dx. \quad (6.29)$$

Positive (negative) values of Q_{NL} signal the occurrence of the bending (squeezing) mode. Unlike the criterion (6.28), the measure (6.29) is applicable to nonlinear stages of the system evolution.

In all numerical experiments the initial bottom layer thickness h_{10} is always 5 nm, and the initial top layer thickness $h_{20} - h_{10}$ is varied (2 nm, 5 nm, 8 nm, and 11 nm for Ag/Co/SiO₂/Si system; 2 nm, 5 nm, and 7 nm for Co/Ag/SiO₂/Si system). Evolution in the non-isothermal systems is computed unless stated otherwise in the figure caption. As we discuss in the following sections, the final nanoparticle morphology can be classified as core-shell, embedded, or stacked structures, as shown in Fig. 6.9. We loosely define the core-shell morphology as one where the maximum deformations of the liquid/gas and liquid/liquid interfaces at the end of the run do not differ by more than 20%, and the embedded morphology as one where this difference is larger. In both cases, the top layer of liquid has to “coat” the bottom layer, in other words, the bottom layer is not exposed to the ambient gas. Stacked morphology can be defined as the limit of core-shell morphology as the thickness of the coating layer tends to zero.

In order to check the code, we compared the instability growth rate from the computations in the early stages of the evolution, when the interfacial deformations are small, with the growth rate from the linear stability theory. Fig. 6.10 shows the comparison for the Ag/Co/SiO₂/Si system and for two grid resolutions. Initially, interfaces are perturbed by a small random perturbation with the maximum amplitude $A_0 = 0.1 \text{ nm}$. It can be seen in Fig. 6.10 that after very short initial transient when the random perturbation somewhat coarsens (not shown), the slopes of the numerical curves for both interfaces become very close to the slope ($= \max(\omega_1)$, see Fig. 6.5) of the straight line (linear theory), and the match improves on finer grid. At later times, i.e. at larger interfacial deformations when the system enters the nonlinear regime, the numerical slopes start to deviate from the linear theory.

All film profiles were computed with increasing resolution until convergence to within 5%; this usually requires 300 - 500 grid points - which is at the limit of our computing power, since resolving the temperature profile is very computationally intensive.

6.4.1 Ag/Co/SiO₂/Si system

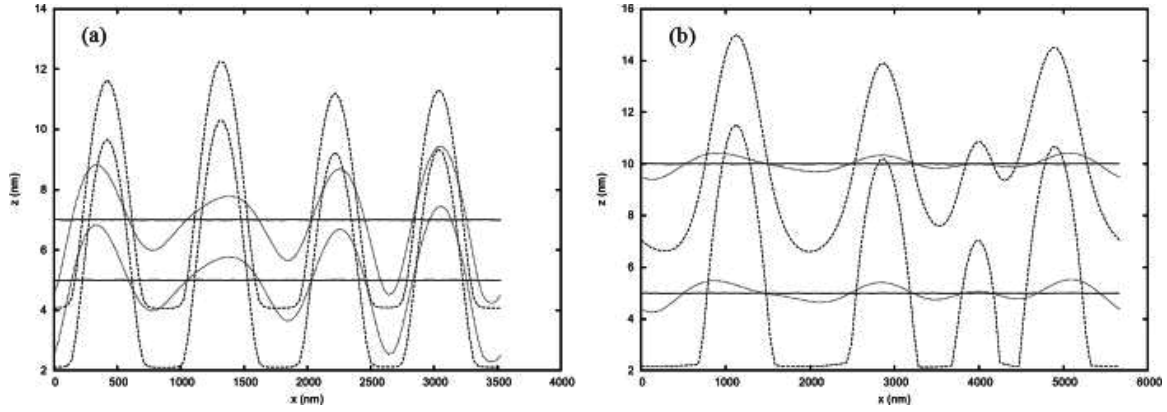


Figure 6.11: Film profiles (core-shell morphology; Ag/Co, coefficient set I). (a) $h_{Co} = 5$ nm, $h_{Ag} = 2$ nm at $t = 0$ (solid line). Dotted line: $t = 1.39 \times 10^{-3}$ s; dashed line: $t = 2.49 \times 10^{-3}$ s. (b) $h_{Co} = 5$ nm, $h_{Ag} = 5$ nm at $t = 0$ (solid line). Dotted line: $t = 4.9 \times 10^{-3}$ s; dashed line: $t = 7.4 \times 10^{-3}$ s.

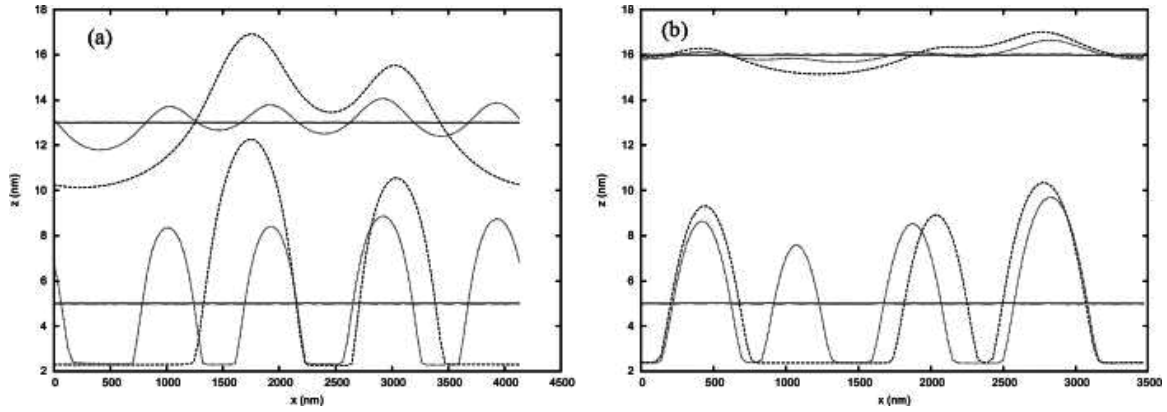


Figure 6.12: Film profiles (embedded morphology; Ag/Co, coefficient set I). (a) $h_{Co} = 5$ nm, $h_{Ag} = 8$ nm at $t = 0$ (solid line). Dotted line: $t = 5.9 \times 10^{-3}$ s; dashed line: $t = 2.99 \times 10^{-3}$ s. (b) $h_{Co} = 5$ nm, $h_{Ag} = 11$ nm at $t = 0$ (solid line). Dotted line: $t = 8.9 \times 10^{-3}$ s; dashed line: $t = 3.11 \times 10^{-2}$ s.

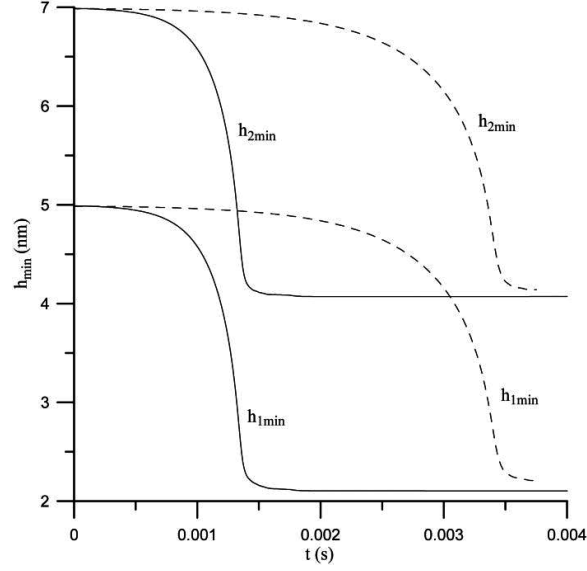


Figure 6.13: Minimum total bilayer thickness h_{2min} and bottom layer thickness h_{1min} vs. time (Ag/Co, coefficient set I). Solid lines: non-isothermal evolution, dashed lines: isothermal one. $h_{Co} = 5 \text{ nm}$, $h_{Ag} = 2 \text{ nm}$ at $t = 0$.

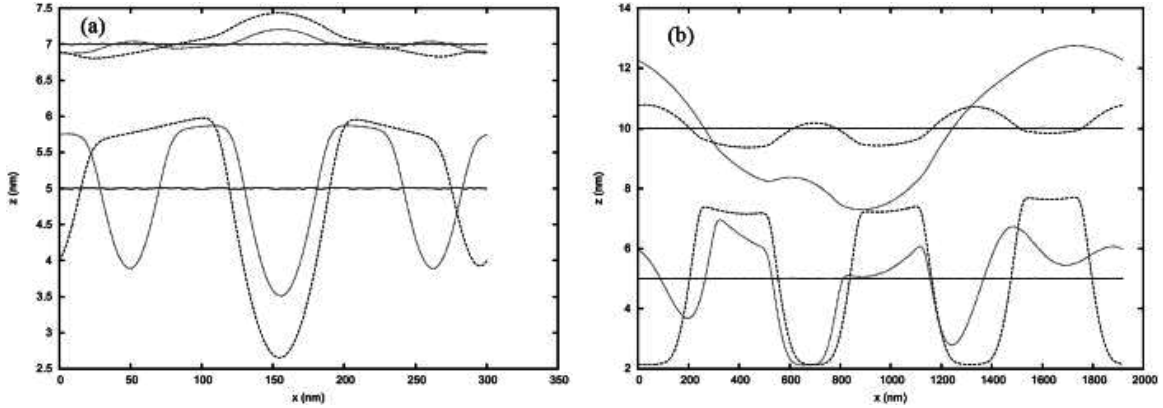


Figure 6.14: Film profiles (embedded morphology; Co/Ag, coefficient set I). (a) $h_{Co} = 5 \text{ nm}$, $h_{Ag} = 2 \text{ nm}$ at $t = 0$ (solid line). Dotted line: $t = 3.9 \times 10^{-6} \text{ s}$; dashed line: $t = 3.42 \times 10^{-5} \text{ s}$. (b) $h_{Ag} = 5 \text{ nm}$, $h_{Co} = 5 \text{ nm}$ at $t = 0$ (solid line). Dotted line: $t = 9.9 \times 10^{-4} \text{ s}$; dashed line: $t = 3.4 \times 10^{-3} \text{ s}$.

As can be seen from Figs. 6.11-6.14 the bilayer evolves in the bending mode for all times, and this is in agreement with the dynamics of polymer bilayer films in case 4 of Ref. [167] within the linear theory's criterion (6.28). Also Q_{NL} (Eq. 6.29) is positive at all times, except sometimes in the early stages of the evolution when the initial roughness starts to coarsen into the four-wavelength profile. After such profile is formed (which is, in fact, four core-shell particles - see Fig. 6.9), its amplitude increases until a wetting layer is formed through the repulsive interaction with the substrate. Then, the profile continues to coarsen until only one large core-shell particle remains. As an example, Figs. 6.13 and 6.14 show coarsening of the four-wavelength profile into a three- and two-wavelength profile. Note that the time scale of the formation

of the four-nanoparticle array in Figs. 6.11, 6.12- 6.14 is of the order of the total irradiation time in the experiments, given that one considers consecutive laser pulses without time delay (that is, $10000 \text{ pulses} \times 10 \text{ ns}$ (the duration of each pulse) $= 10^{-4} \text{ s}$).

As Figs. 6.12-6.14 demonstrate, with the increase of the Ag thickness the evolution of the Ag layer slows down significantly, resulting, for the sufficiently large Ag thickness, in the formation of Co particles embedded in the Ag matrix. The transition from core-shell particles to embedded ones occurs for Ag layer thickness between 6 and 8 nm.

The nonlinear evolution in the isothermal case does not differ significantly from the just described non-isothermal evolution. That is, the bilayer evolves in the bending mode at all times and core-shell particles form for the Ag layer thickness less than 6 - 8 nm, while embedded Co particles form for the larger Ag layer thickness. Of course, in accord with the linear stability analysis, see Fig. 6.6, the particle spacing (before coarsening occurs) is larger than in the non-isothermal case. Isothermal evolution is much slower than the non-isothermal one (Fig. 6.15) due to a capillary effect, i.e. the larger surface tensions ($\sigma_{1,2}^{(m)}$) compared to the non-isothermal one, Eqs. (6.11) and (6.12). This is generic for all nonlinear examples in this paper.

6.4.2 Co/Ag/SiO₂/Si system

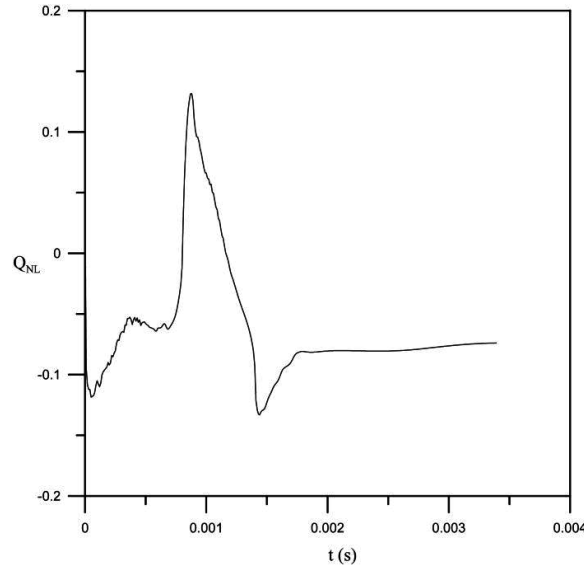


Figure 6.15: Monitor function for the evolution in Fig. 6.14(b).

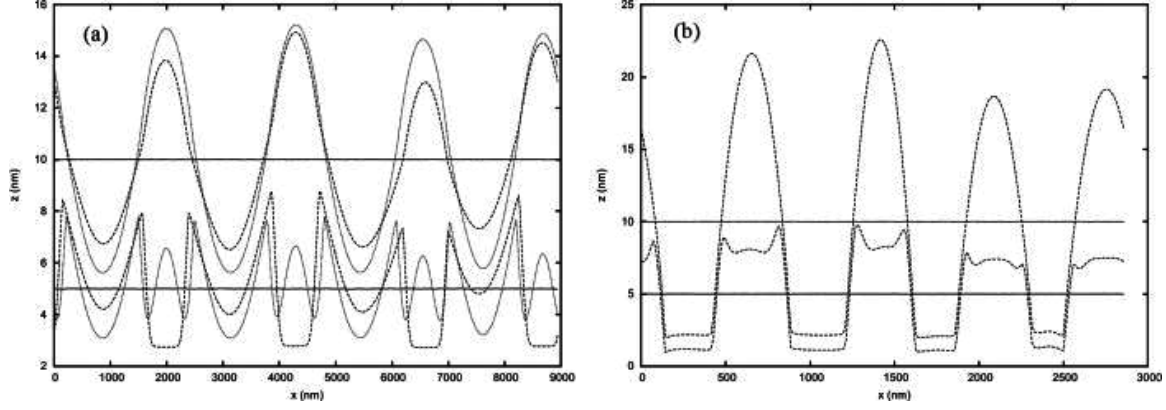


Figure 6.16: Film profiles. (a) Core-shell morphology; Co/Ag, coefficient set I, isothermal strong repulsion. $h_{Ag} = 5 \text{ nm}$, $h_{Co} = 5 \text{ nm}$ at $t = 0$ (solid line). Dotted line: $t = 1.07 \times 10^{-3} \text{ s}$. Dashed line: $t = 4 \times 10^{-3} \text{ s}$. $S_1 = -14 \frac{\text{J}}{\text{m}^2}$, $S_2 = -40 \frac{\text{J}}{\text{m}^2}$ (b) Stacked morphology; CoAg, coefficient set II, $h_{Ag} = 5 \text{ nm}$, $h_{Co} = 5 \text{ nm}$ at $t = 0$ (solid line). Dashed line: $t = 7.7 \times 10^{-6} \text{ s}$.

For the first set of the Hamaker coefficients the solution starts in the squeezing mode as predicted by Eq. (6.28), and then either continues in this mode for a thin Co film, or passes through the several periods of bending before settling in the squeezing mode for the thicker Co film. Figs. 6.16 and 6.17 show the film profiles for $h_{Co} = 2 \text{ nm}$ and 5 nm , respectively. Fig. 6.15 shows the monitor function (6.29) for the latter case. It is clear from these figures that dewetting rate is significantly smaller than the rate of particle formation and coarsening, thus the Ag particles form on the surface of a thick Ag wetting layer, capped by the (almost planar) Co layer. The resulting morphology falls into “embedded” class.

Under isothermal conditions the deformation mode is also squeezing for $h_{Co} = 2 \text{ nm}$ (and the morphology is similar to Fig. 6.16), but for thicker Co film it is bending. However, there is no particle formation in this latter case, since the Co layer dewets much faster than the Ag layer, and the bilayer ruptures when the Co/air interface reaches the Ag/Co interface. Such rupture can be prevented only by larger intermolecular repulsive forces between the interfaces; in this case, the rate of Co interface coarsening is much smaller than the rate of Ag interface coarsening, which results in multiple particles of Ag coexisting within the single particle of Co; this distinct embedded-type morphology is shown in Fig. 6.18. *When the interlayer repulsion is strong, same morphology occurs in the non-isothermal situation as well.* Note that in agreement with the analysis of Bandyopadhyay *et al* [167], no switching from bending to squeezing, or vice versa occurs in the isothermal situation.

For the second set of the Hamaker coefficients the evolution is entirely in the bending mode and is quite similar to the Ag/Co/SiO₂/Si system. Fig. 6.16 shows one such morphology. By comparing to Fig. 6.12, one can notice that in the Co/Ag/SiO₂/Si system much smaller particles are formed from the bottom layer material and the shell (the top layer material) is thick at the top but very thin at the sides, while in the Ag/Co/SiO₂/Si system it is the opposite. In the real physical system, one expects point rupture (for instance, due to thermal fluctuations) of the Co layer at the side wall of the Ag particle, which results in the stacked morphology.

6.5 Bilayer thermal model

The process of bilayer heating due to repetitive laser pulses of nanoseconds duration is described in 2D by:

$$\rho C_p \frac{\partial T}{\partial t} = \nabla[k \nabla T] + Q_{laser}(y, t) + Q_m \frac{dy_i}{dt}. \quad (6.30)$$

Here the source terms account for laser heating and melting/freezing, C_p is the isobaric heat capacity, Q_m is the heat of melting of thin metal layers, and $\frac{dy_i}{dt}$ is the rate of displacement of the solid/liquid interface located at y_i . (y is the axis normal to the planar, fixed surface pointing inward the material.)

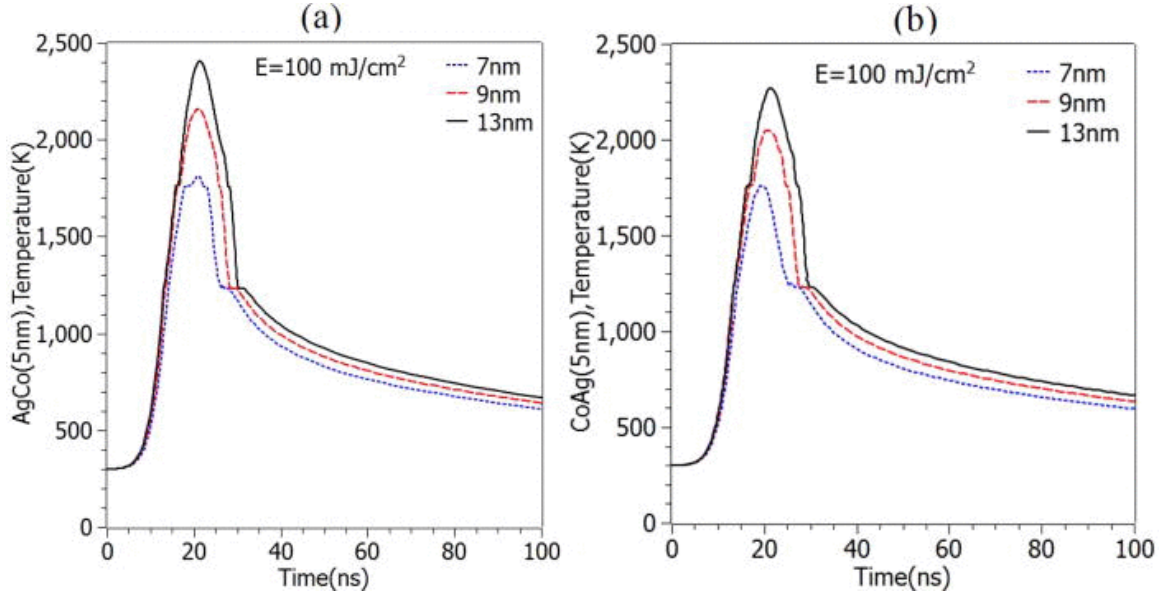


Figure 6.17: (a) Temperature of Ag/Co/SiO₂/Si system vs. time. (b) Temperature of Co/Ag/SiO₂/Si system vs. time. Figure shows the total bilayer thickness, and the quantities plotted correspond to a single laser pulse.

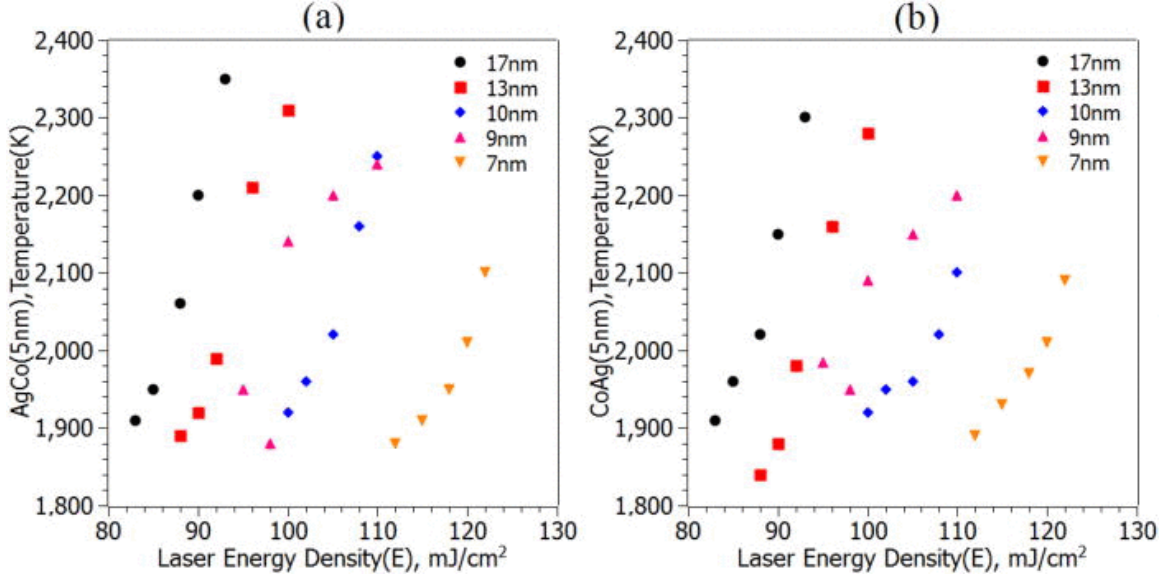


Figure 6.18: (a) Temperature of Ag/Co/ SiO₂/Si system vs. the laser energy density. (b) Temperature of Co/Ag/SiO₂ /Si system vs. the laser energy density.

$Q_{laser}(x,y,t)$, the laser heating contribution, is given by

$$Q_{laser}(y,t) = A(y)(1 - R(y))I(t)\exp(-A(y)y), \quad (6.31)$$

where $R(y)$ is the thickness dependent reflectivity, and $A(y)$ is the thickness dependent absorption coefficient. Both the reflectivity and the absorption coefficients are calculated using the method described in Ref. [218]. The incident laser power has Gaussian distribution:

$$I(t) = \sqrt{\frac{2}{\pi}} \frac{E}{\sigma} \exp\left(-\frac{2(t - \delta)^2}{\sigma^2}\right) \quad (6.32)$$

where $\delta(18ns)$ is the time at which the maximum intensity is reached and $\sigma(9ns)$ the width of the pulse. E , the laser energy density in mJ/cm². For the system given by film 1/film 2/SiO₂/Si, the above The above heat equation was subject to the following boundary conditions:

(a) Sides are thermally insulated, and $T(y=h_{Si},t)=T_0$, where h_{Si} is the bottom of the substrate and $T_0 = 300$ K

(b) $T(y,t=0)=T_0$ at all interfaces.

(c) At interior boundaries/interfaces heat flow is taken as continuous ($k_{y1}\nabla T_1 = k_{y2}\nabla T_2$)

(d) Thermal radiation heat transfer at the top surface is neglected, as justified in [37].

The results were computed using the finite element software (FLEX-PDE). Figures 6.17-6.18 show the various quantities calculated.

In this chapter we showed how the internal forces and thermal gradients come together to control the morphology of bimetal nanoparticles.

Chapter 7

Conclusions and future work

7.1 Conclusions

In this chapter, we summarize the key findings of this thesis and speculate on some future directions for research based on the results obtained during this study. We reported the detailed study on the novel patterning techniques and understanding instabilities in Single and Bilayer systems. The scientific motivation and technological significance of this work were addressed in detail in the introductory chapter (Chapter 1) of the thesis. The highlights of this research work are as following:

- Chapter 2: In conclusion, the thickness dependence of dewetting pattern evolution in Au thin films was studied in the range of ~ 3 to 16 nm under nanosecond pulsed laser melting. Investigations of the dewetting morphologies show that Au has bicontinuous structures for film thickness ≤ 8.5 nm and hole-like structures for film thickness ≥ 10 nm. Evaluation of the trend in characteristic length scales as measured by inter-particle spacing λ and diameter D shows the classical h^2 and $h^{5/3}$ dependence respectively, confirming that Au follows classical spinodal dewetting behavior. Evaluation of the thermal gradient forces under the transient laser heating confirmed that thermocapillary forces in Au are significantly weaker than its dispersive forces. Au was observed to have a very large Hamaker coefficient and as a result the Au dewetting length scales are significantly smaller than of other metals such as Ag and Co. Nonlinear modeling studies show very good correlation with experiment in capturing the 3-dimensional morphology of the dewetting Au films as well as in the evolution of this morphology. These studies lay the foundation of accurate computer-driven design of pulsed laser dewetting nanostructures for future implementation in nanomanufacturing scenarios.
- Chapter 3: In this work we show a new way to synthesize nanoparticle arrays on a substrate with independent control of size and spacing, while also overcoming the limitations of self-organized length scales. The approach is based on applying the Rayleigh Taylor instability to the nanoscale, a first such demonstration, since this instability, thus far, has only been observed in macroscopic systems. Theoretical arguments suggest that when thin films are rapidly melted inside a bulk fluid, the ensuing gas pressure gradients can produce huge acceleration forces that can destabilize the film leading to the RT instability and predictable nanoscale sizes. Experimental studies performed for nanosecond pulsed

laser melting of Au films in glycerol agreed with the theory. Nanoparticles with a highly monomodal size could be synthesized. Importantly, the spacings between nanoparticles was independent of the film thickness and depended primarily on the pressure gradients, which could be controlled by the laser energy. Since the theory underlying this nanoscale Rayleigh-Taylor instability appears independent of the type of thin film material and/or substrate, this technique could be widely applied to synthesis of nanoparticles from many different materials classes i.e. polymers, ceramics or metals.

- Chapter 4: In conclusion we have discovered a new *phase array* self-assembling phenomenon in which a DC electric field applied to an insulating substrate can control the periodic pattern formation of metallic nanoparticles under polarized laser irradiation. A near-random distribution of Au nanoparticles can spontaneously assemble into a one dimensional periodic arrangement with extremely low misorientation defects, producing a single-crystal-like spot diffraction pattern. The underlying role of the electric field appears to be to change the phase between the radiation scattered by the individual nanoparticles. While this phase array effect is widely used in radar and antenna applications, it is the first demonstration of this concept in the nanoscale, and especially to self-assemble materials. This simple approach could be very useful towards fabricating metal nanoparticle arrays over large areas with a high degree of one dimensional periodic arrangement.
- Chapter 5: We have investigated the early stage ripening morphologies and morphology transitions in bi-layer spinodal dewetting systems made from Ag/Co and Co/Ag bilayers on SiO₂ surfaces. By varying the individual film thickness and investigating the dewetting morphology following nanosecond pulse laser melting for various film thickness cases, we have experimentally constructed the phase diagrams for the bi-layer dewetting systems. Analogous to single-layer dewetting, the bi-layer systems only show either the characteristic bicontinuous or hole-like morphologies as a function of varying thickness. However, unlike the single-layer films, multiple morphology transitions may occur. Based on analysis of the free energy curvature, we determined that bi-layer systems only partially follow the curvature minima and morphology relationship found in single-layer films, in which the minima determined the location of the films transition thickness and this was always from a bicontinuous (to the left of the minima) to a hole-like (to the right of the minima) morphology. For the bi-layer case, the minima represents one of the possible transitions and could either be a bicontinuous to hole or a hole to bicontinuous transition. However, the bi-layer phase diagram can be completely described by the location of the two single-layer film transitions that make up the system. Therefore, despite the complexity of the non-linear evolution of the morphology in bi-layer dewetting systems, one can easily construct the complete morphology phase diagram from the behavior of the individual single-layer films. The result can help improve the speed and accuracy of non-linear modeling of such pattern forming phenomenon and also help to fabricate multi-elemental nanomaterials with morphologies that could show useful physical properties.
- Chapter 6: In this paper, the nanostructure-forming dynamics in pulsed-laser irradiated Ag/Co and Co/Ag thin bilayer films on an optically transparent substrate with a reflective support layer has been studied by means of a 2D linear stability analysis and nonlinear simulations. The long-wave ap-

proximation is employed. The full heat conduction problem, which includes the thickness dependent reflectivity and absorption in the bilayer is formulated, solved exactly, and the solution is coupled to the evolution equations for the thickness functions of the two layers. Intermolecular forces are accounted for in the evolution equations, and the thermocapillary (Marangoni) effect resulting from the thickness-dependent temperature is also taken into account at the gas-liquid and liquid-liquid interfaces. Linear stability analysis provides the nanoparticle spacing as a function of a thickness of a top layer. A better prediction of the experimental length scales was found for the non-isothermal calculations as compared to the isothermal case. This is a strong indication that thermocapillarity plays an important role in nanopatterning of laser-irradiated metallic bilayers. In the simulations, different pathways to core-shell, embedded and stacked nanoparticle morphologies were identified. These pathways are through the bending or squeezing evolution modes. The Ag/Co system evolved in the bending mode and core-shell nanoparticles form at the small-to-medium thicknesses of the top Ag layer; particles of Co embedded in the Ag matrix form at the large thicknesses of the Ag layer. The Co/Ag system may evolve in either a bending, or squeezing, or mixed mode, depending on the strengths of the intermolecular forces and the layers thicknesses. The squeezing and mixed modes lead to large embedded Ag particles. The bending mode most often leads to Co particles stacked on top of Ag particles. For both systems, isothermal evolution and outcomes were distinctly different, which once again emphasized the critical importance of the thermocapillary effect..

7.2 Future directions

7.2.1 Break up of bicontinuous nanostructures: Role of laser energy

Ag films of thickness 6 ± 0.5 nm were deposited in high vacuum ($\sim 1 \times 10^{-8}$ Torr) by electron beam deposition at room temperature onto transparent Quartz substrates. The wafers were cleaned in methanol, acetone, and DI water. The deposition rate used here was typically ~ 1.5 nm/min as confirmed by atomic force microscope (AFM) step height measurements of the film thickness. The surface roughness of the deposited films were measured by AFM and was established to be 0.5 ± 0.2 nm for the average root mean square (RMS) roughness.

The laser irradiation was performed in two stages. First, the deposited Ag films were raster scanned by a 266 nm ultraviolet laser having a pulse width of 9 ns. Irradiation was performed in air ambient and at normal incidence by an unfocused laser beam of area 1×1 mm² with a scan rate of $0.5 \frac{cm}{min}$ at a repetition rate of 50 Hz. The laser energy density used was $E = 35$ mJ/cm², which is very close to E_{Melt} . This irradiation step resulted in a spaghetti or bicontinuous nano structures (BCN) due to the phenomenon of spinodal dewetting. This stage 1 BCN was characterized by scanning electron microscopy (SEM) and is shown in Fig. 7.1(a). The samples having similar BCN morphology as characterized by the radial distribution functions Fig. 7.1 (b). The samples that show similar radial distribution function were selected for the stage two laser irradiation experiments. In stage 2, the Ag BCN obtained in stage1 on Quartz substrate were immersed in de-ionized water. The samples were then re-irradiated with linearly polarized (P) laser light with an energy density $30 \leq E \leq 80 \frac{mJ}{cm^2}$. Following the irradiation, the samples were removed from water, dried in air, and

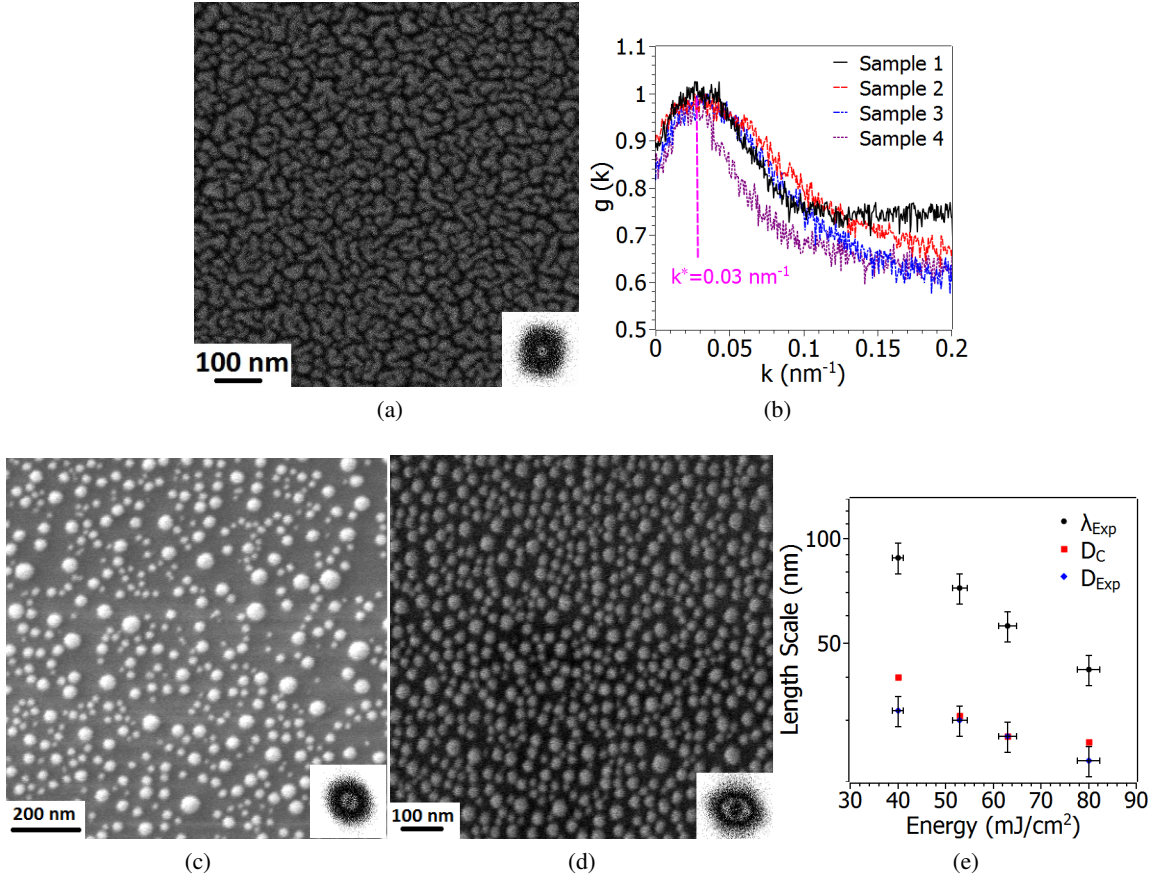


Figure 7.1: (a) SEM image of the early stage dewetting BCN morphology following irradiation by raster scan of 6 nm Ag film in air. (b) Plot of the radial distribution function (RDF) for different control BCN samples prepared by raster scan. (c-d) Short range ordered Ag nanoparticles obtained by irradiating BCN in de-ionized water at laser energy density $E = 40 \frac{mJ}{cm^2}$ and $E=80 \frac{mJ}{cm^2}$. (e) Analysis of the various length scales and diameters in the final nanoparticle state for various laser energy densities. D_c is the theoretically calculated diameters from the experimentally observed length scales using volume conservation.

the resulting nanostructures were investigated in a scanning electron microscope (SEM).

7.2.2 Break up of bicontinuous nanostructures: Role of fluids

Au films of thickness 6 ± 0.5 nm were deposited in high vacuum ($\sim 1 \times 10^{-8}$ Torr) by electron beam deposition at room temperature onto transparent Quartz substrates. The deposited Au films were raster scanned by a 266 nm ultraviolet laser having a pulse width of 9 ns. Irradiation was performed in air ambient and at normal incidence by an unfocused laser beam of area 1×1 mm² with a scan rate of $0.5 \frac{cm}{min}$ at a repetition rate of 50 Hz. The laser energy density used was $E = 40$ mJ/cm², which is very close to E_{Melt} . This irradiation step resulted in a spaghetti or bicontinuous nano structures (BCN) due to the phenomenon of spinodal dewetting. This stage 1 BCN were characterized by scanning electron microscopy (SEM) and is shown in Fig. 7.2(a). The samples having similar BCN morphology as characterized by the radial distri-

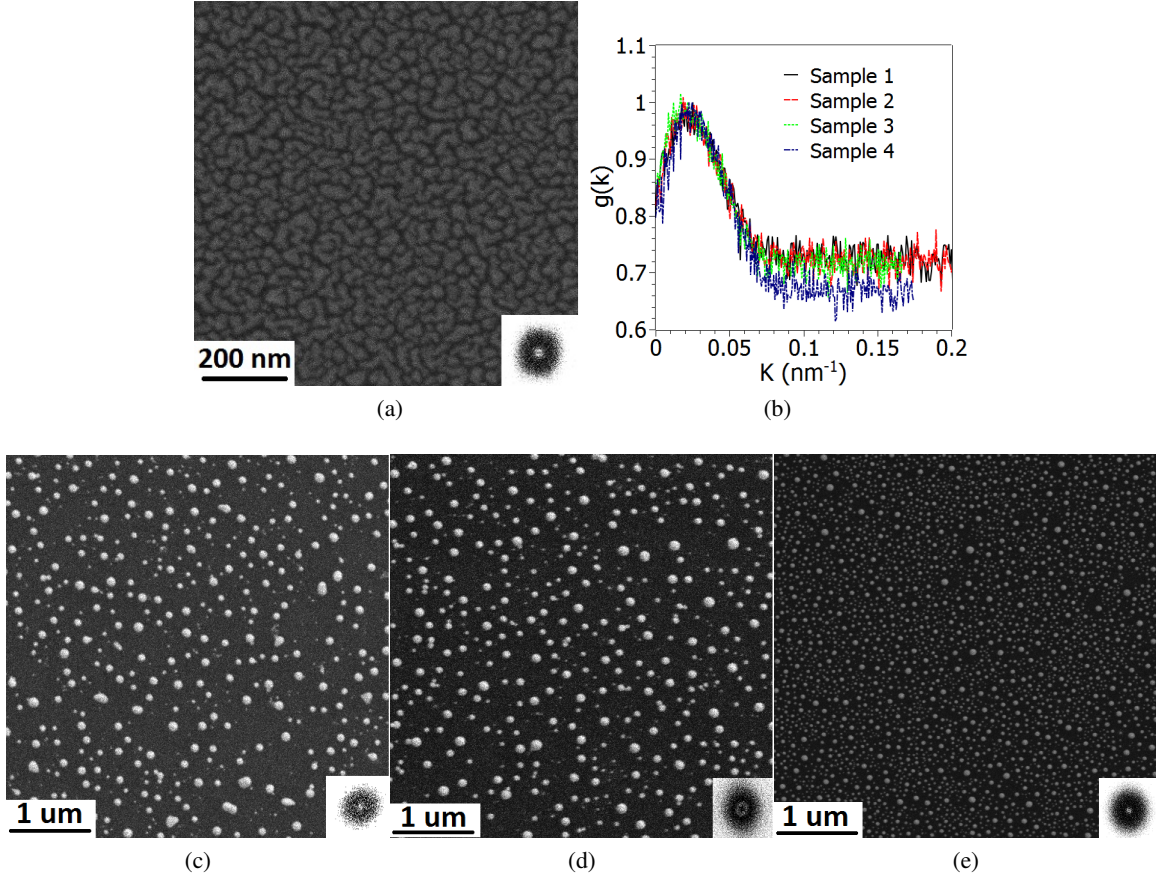


Figure 7.2: (a) SEM image of the early stage dewetting BCN morphology following irradiation by raster scan of 6 nm Au film in air. (b) Plot of the radial distribution function (RDF) for different control BCN samples prepared by raster scan. (c-e) Short range ordered Au nanoparticles obtained by irradiating BCN in water-glycerol homogeneous mixtures (100% water, 50%water+50%Glycerol, 100% Glycerol) at laser energy density $E = 70 \frac{mJ}{cm^2}$.

bution functions Fig. 7.2 (b) were selected for the stage two laser irradiation experiments. In stage 2, the Au BCN's obtained in stage1 on Quartz substrate were immersed Gold-Glycerol mixture solutions. The samples were then re-irradiated with linearly polarized (P) laser light with an energy density $E = 70 \frac{mJ}{cm^2}$. Following the irradiation, the samples were removed from fluid, dried in air, and the resulting nanostructures were investigated in a scanning electron microscope (SEM).

7.2.3 Bilayer dewetting in presence of liquids

Self organization of bilayers in liquids is investigated in this work. AgCo films of thickness Ag (5nm) on Co (5nm) was deposited on transparent bulk quartz (SiO₂) substrates. The deposition rates for both Co and Ag used here was typically ~ 1.5 nm/min as confirmed by atomic force microscope (AFM) step height measurements. The Ag/Co/SiO₂ samples were positioned in a beaker filled with deionized water. Laser irradiation was performed at normal incidence from the quartz side with an unfocused laser beam of area 1×1 mm² at a repetition rate of 50 Hz for a total of 5000 pulses. Following the irradiation, the samples

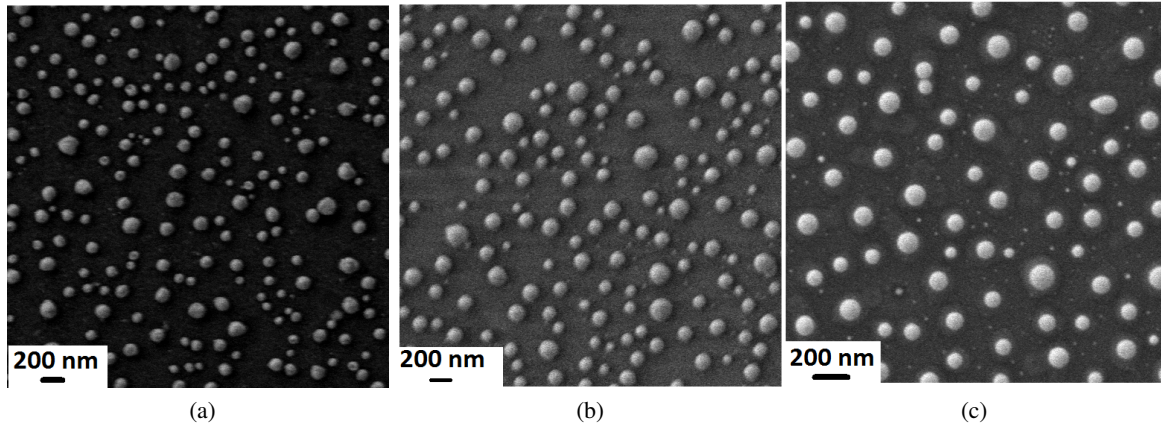


Figure 7.3: (a-c) SEM images of AgCo nanoparticles obtained by irradiating Ag(5nm)/Co(5nm)/SiO₂ in water at laser energy densities 70, 90 and 120 $\frac{mJ}{cm^2}$

were removed from the fluid, dried in air, and the resulting nanostructures were investigated in a scanning electron microscope (SEM) as a function of laser energy density E .

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