A Thesis

entitled

Fabrication of Metal Microstructures by Single-Pulse, Localized Irradiation of Thin Metal Films

by

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This thesis deals with the formation of microbumps and high-aspect-ratio protrusions on gold, copper, titanium, aluminum films as a result of single-pulse localized laser irradiation. A Q-switched nanosecond-pulse laser, emitting at its fourth harmonic of 266nm was the laser source employed and a demagnifying projection optical system was used to produce micrometer-scale circular laser-irradiation spots. Gold, copper, titanium and aluminum films with a thickness of several hundred nanometers were irradiated, under low-vacuum conditions, with circular laser spots that were several micrometers in diameter. The metal films were deposited by RF or DC sputtering from the corresponding metal targets. The resulting structures were imaged via scanning electron microscopy. The formation mechanism of these structures is briefly discussed in view of our results and other, related published work.

We studied the conditions for pulsed laser micro structuring of metal films on various substrates, with main focus on determining fluence levels and irradiation geometry parameters in which the formation of various substrates is possible in a reproducible fashion. The laser-deposited heat transfer within the irradiated films was
evaluated using the COMSOL finite-elements modeling software, and the resulting temperature profiles are discussed in the context of the experimentally obtained results.
I dedicate this thesis to my parents Gopal Reddy and Premalatha and my brother Bhanu Prakash. I am grateful to them for all their sacrifices. Their endless love and support have given me the confidence to move ahead and face every challenge I have.
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Chapter 1

Introduction

Single pulse nanosecond localized irradiation of thin metal films can result in the formation of sharp protrusions or other types of microstructures. Such irradiation can be performed under different conditions such as pressure, vacuum and argon with different mask sizes at different fluence levels. Of interest to this project is pulsed laser micro structuring of metals such as Au, Cu, Al, Ti which represents a large range of melting points and chemical reactivity levels. Potential applications of such microstructured metal films and surfaces include: field emission, vacuum microelectronics, sensors, biomedical device fabrication, surface-enhanced Raman spectroscopy and related applications [1,2]. Laser micro structuring is an attractive approach in such applications, among various alternatives. In the area of vacuum microelectronics, specific applications include: emitters for field-emission based devices, such as high-definition displays, flat panel displays[3,4] as well as microwave amplifiers, [5,6,7] traveling wave tubes, klystrons etc. Micro electro mechanical system (MEMS) based memory devices that use sharp large moveable arrays of sharp microtips to access individual phase-change cells can benefit from new fabrication methods for sharp tips as well as thermomechanical storage media,[8,9] antireflective surface structuring,[10,11] and surface engineering for
biomedical implant devices[12,13,14]. Another potential application is the use of high-
surface area micro- and nano-structures of high thermal conductivity materials to enhance
heat transfer (i.e. cooling).

Laser –assisted or direct-laser fabrication methods represent an attractive alternative
to conventional methods, such as lithography. Technological tools that provide a means
of working at the micrometer and submicrometer level are becoming more and more
important. The most common strategy to build such a tool is to improve a reliable
microstructuring technology in terms reduction of structural dimensions. In optical
lithography, which is, the most widely used micrometer and submicrometer scale
structuring technology today, the reduction of feature sizes is achieved mainly by using
shorter wavelength light. This technology is predicted to be applicable not much beyond
100 nm. It is also not a universal technology. It can be applied only on a limited set of
materials and on plane surfaces. Therefore, the development of other submicrometer-
structuring technologies remains necessary [15]. There are laser irradiation techniques
that are considered attractive alternative to conventional methods of micro-and nano-
structuring. Among these, single-pulse laser based techniques have received an attention,
which is increasing over the last decade.

The main advantages of laser-based approaches include: local processing down to
the micrometer and even submicrometer range, high throughput, minimized thermal
damage to the substrate and neighboring regions, noncontact nature, nonplanar
processing, and the possibility of combining it with other types of processing such as
surface chemical treatment and film deposition steps [16].
In this thesis, we describe and analyze results on obtaining sharp micro structures, round-top microbumps and other shapes by micrometer scale localized single-pulse nanosecond laser irradiation of thin metal films on various substrates. Deposition of the metal films was performed by DC or RF sputtering. The resulting structures were characterized by techniques such as scanning electron microscopy (SEM). We studied conditions for pulsed laser micro structuring of metal films on various substrates, and our research focuses on determining fluence levels and irradiation geometry parameters in which the formation of various substrates is possible in a reproducible fashion. We also studied relations between structure size, laser fluence and film thickness, and irradiation atmosphere.

**Problem Definition**

As mentioned earlier, micro- and nano-structuring of metal film surfaces is of interest to applications which include emitters for field-emission based devices, such as high-definition displays as well as other vacuum microelectronics devices and systems micro electro mechanical system (MEMS) based memory devices and surface patterning of materials for biomedical applications. It has been established that using single-pulse nanosecond, localized irradiation of Au film can result in the fabrication of various sharp, high-aspect ratio of various tip micro/-nanostructures while providing relatively high throughout and formation fluence [17].

In this project, we examine the possibility of micro-/nanostructures of other metal films in a similar way. The metal films which were subjected to irradiation experiments include Cu, Ti, Al. In addition we further examine the formation of structuring on Au,
specifically in the case of very thick (greater than 1um) Au films. Pulsed laser structuring of thick Au and thin Au on borosilicate glass (BSG), Si is done in various conditions such as pressure, vacuum, argon gas.

In addition to Au and Cu we examine the possibility of forming micro-/nanostructures on metal films like Ti, Al with irradiation, performed under a range of conditions, upon varying parameters like spot size, atmosphere, film thickness, and fluence levels. The resulting structures were characterized using scanning electron microscopy. The main goal was to see if single-pulse laser microstructuring of such is possible, and then identify the relevant parameter space.
Chapter 2

Literature Review

2.1 Relevant Microfabrication Techniques

Fabrication of nano-tips and micro-bumps can be done by different methods such as

2.1.1. Lithography based techniques.

2.1.2. Chemical vapor deposition.

2.1.3. Multi-pulse laser irradiation.


2.1.5. Laser Induced Forward Transfer (LIFT) and related methods.

Each method has its own advantages and disadvantages, but the single pulse laser irradiation which is of interest to this project has many advantages such as low cost, simplicity, control over the structures shape and location.

2.1.1. Lithography based techniques

The various steps involved in the lithography based fabrication process are deposition, patterning and etching. These processes can be performed multiple times, in various orders to produce the desired structures. These kind of methods are capable of forming many types of structures, and offer high precision, resolution and repeatability.
These advantages however, come at a high cost in terms of required facilities their maintenance. In addition, lithography based processing is intrinsically planar in nature and therefore of somewhat limited flexibility. High-temperature processing is also often needed and this is not desirable.

Examples of relevant lithography based fabrication are given next. Field emitter array (FEA) have been prepared on a silicon substrate by lithographic techniques similar to those used in the fabrication of integrated circuits [18]. In their original form, FEAs consisted of the *Spindt-type emitters*, in which the individual field emitters are gated, sharp molybdenum cones [19,20]. Each is deposited inside a cylindrical void in an oxide film, with a closely spaced electrode film deposited on the top of the oxide film. This electrode (called the "gate") is patterned in the shape of a separate circular aperture for each conical emitter tip. The device is named after Charles A. Spindt, who developed this technology. Because it has a sharp apex, a Spindt tip locally enhances the electric field allowing emission of electrons in vacuum (field emission or cold-cathode emission) at relatively low gate voltages (less than 100 V). By using a complex sequence of lithography, and film deposition, the individual emitters can be packed close together in large arrays [21]. However, the complexity of the fabrication method, and related scaling-up issues have limited the success and prevented the commercialization of this technology. The basic fabrication process is given next and illustrated in Figure 2.1.1-1. The formation of these structures begins with the creation of a cavity, like that in Figure 2.1.1-1(a), produced via photolithography, etching and deposition. A sacrificial (lift-off) layer is deposited onto the surface as seen in Figure 2.1.1-1(b). The tip material is then deposited at two different angles, to fabricate the cone in Figure 2.1.1-1(c). Material
deposited normal to the substrate forms the cone, while the material deposited at a grazing angle with respect to the substrate is used to close the cavity. The grazing angle and deposition rate of the second deposition source determines the closure rate and therefore, the height and angle of the resulting tip. Finally, the lift-off material is removed using a solvent or etchant which only attacks the lift-off material (2.1.1-1(d)).

Figure 2.1.1- 1: Spindt array formation method [22].

Sharp silicon tips are fabricated by a combination of lithography based patterning and etching steps. In the work, reported in ref. [18], silicon tips were created via a two step etching processes; which begins with the anisotropic etching in a potassium hydroxide (KOH) solution, followed by a SF6 plasma etching.

2.1.2 Chemical vapor deposition

Chemical vapor deposition is a chemical process used to fabricate high-purity, high-performance solid materials. The process is used in the semiconductor industry to produce thin films. This process uses a volatile gaseous precursor, which is passed over a
heated substrate. As the precursor comes in contact with the substrate, it reacts and/or decomposes onto the surface. There are many variants to this process including, radio-frequency plasma enhanced CVD (RF-PECVD), hot-filament CVD (HF-CVD), thermal CVD (T-CVD), metal organic CVD (MO-CVD) and microwave plasma enhanced CVD (MW-PECVD) as well as others [23]. Each of these variants offers different advantages when depositing a particular material. While this method can be used to create impressive looking nano-tips, without the use of pre-patterning or specialized catalyst deposition tips such as in [24], there is no control over the location of the tips [23]. This method also requires high substrate temperatures, which limits its applications to temperature insensitive devices.

The CVD method can be used to form nano-tips and nano-rods using variety of materials. For example ZnO nano-wires and nano-rods are grown vertically on Si substrates by nano-catalytic vapor-phase epitaxy [25]. In Figure 2.1.2-1 we present metal organic chemical vapour deposition (MOCVD) of vertically well-aligned ZnO nano-needles on Si substrates and their structural and optical properties. The surface morphology of as-grown ZnO nanoneedles on Si substrates was investigated using scanning electron microscopy (SEM) [25].
2.1.3 Multi-pulse laser irradiation

Multi-pulse laser irradiation techniques employ hundreds or thousands of laser pulses to cause repeated ablation and re-deposition of material, resulting in the formation of various sharp structures. These types of methods offer relatively high throughput and low cost compared to other methods. However, these techniques do not provide direct control over the location of the resulting individual tips and only a limited control over the height and shape of each tip is possible. Since this method requires irradiation of a relatively large area, it is not possible to form one single tip, only large arrays of tips with random distributions.

Dense arrays of high-aspect-ratio silicon microcolumns have been shown to form via nanosecond irradiation using a KrF excimer laser in oxidizing atmospheres [26]. The
effect of femtosecond and nanosecond laser regimes on the structure formation has been examined in [27]. Still other arrays of silicon microcolumns have been shown to form by nanosecond irradiation of a silicon sample with a 500 μm diameter beam using an ArF excimer laser (λ = 193 nm, τ = 23 ns) in air [28]. These microcolumns form after hundreds of laser pulses at a fluence of 2 J/cm² [29]. The resulting structures are generally larger, more rounded and appear to have a smoother surface than those previously mentioned. This may be due to the formation process, which is thought to occur not from ablation and re-deposition, but instead via hydrodynamical forces [28, 29].

2.1.4 Single-pulse laser irradiation

The single-pulse laser irradiation uses a single laser pulse focused onto the sample surface to create localized melting and/or deformation. To overcome some of the limitations that multi-pulse laser irradiation has, and at the same time maintaining the advantages of laser processing, a formation method using a single laser pulse has been developed. This technique has seen considerable interest in recent years, and has been applied to the processing of both semiconductor and metal thin films [30,31,32].

2.1.5 Laser Induced Forward Transfer (LIFT) and related methods

The LIFT method for fabrication of micro and nanostructures on a substrate is relevant to our work in two different ways. First, it is an alternative method for controllable fabrication of individual structures as well as arrays of them, and second, it is a laser based method in which the irradiation geometry and the resulting processes share
common features with our single-pulse method. The LIFT method is briefly described next, together with some examples. LIFT belongs to the class of deposition methods, which utilize lasers to transfer a thin material layer with a resolution in the micron range from a target to a receiver material. Many different modifications of this approach exist which vary in the utilized laser, additional materials, or the conditions, e.g., vacuum [33,34,35,36].

LIFT involves the pixellated transfer of material from a thin film coated onto the rear side of a transparent support substrate. Transfer is induced by focussing one or more laser pulses onto the support-film interface, where heating and phase change of the film provide the propulsion to propel material to a receiving substrate placed nearby. The technique is particularly interesting due to its simplicity and versatility for micropatterning of a range of materials onto unconventional substrates and geometries.

Since this project deals with micro-structuring of metal films, it is important to review the metals of deposition of such films. The deposition techniques are usually divided into physical (e.g., PLD) and chemical (e.g., CVD) methods. Thin films are prepared from inorganic, organic or even biological materials and are nowadays applied as protective coatings, decoration, as structural and electronic materials and in optics (e.g., mirrors), etc., while the most important polymeric materials are photoresists (deposited by spincoating). Recently, the deposition of sensitive organic/polymeric (multi-)layers and biological samples became also an important research topic [37].
Other relevant study includes, the ablation process was achieved and the dependence of the laser spot size on the resolution of a deposited material was revealed by a single pulse of KrF excimer laser (wavelength: 248nm, pulse width: 30ns) with flat-top profile of LIFT set-up using mask projection method [38].

2.2 Potential applications of laser-fabricated sharp tips, microbumps, and other types of laser microstructured of metal films

Sharp conical tips with heights of hundreds to thousands of nanometers and diameters from hundreds of nanometers to several micrometers (referred to as nanotips) have many useful applications which include:

2.2.1 Emitters for field-emission based devices

Field emission (FE) is the emission of electrons from the surface of a condensed phase into another phase due to the presence of high electric fields. In this phenomenon, electrons with energies below the Fermi level tunnel through the potential barrier at the
surface, which the high electric field sufficiently narrows for the electrons to have a non-negligible tunneling probability [18,39]. As a result emission of electrons from a normal surface would be difficult so, sharp protrusions are made so that electrons can be removed easily by applying less electric field.

2.2.2. Biomedical applications

Titanium metal and its alloys are of high interest for biomedical applications [40] owing to their unique properties. Although optimization of bulk properties has for a long time received attention, providing high fatigue resistance and low modulus, only recently has optimization of surface properties been examined systematically [41,42,43]. Titanium-implant surfaces are subject to long-term corrosion, potentially triggering inflammation and toxicity, and are required to provide good biointegration and bioconduction. In other words, they must play an active role in the development and life of the surrounding tissues (bone for instance) without causing any disturbance to the biological functioning [44].

Micro-structured silicon and metal surfaces are also of interest to biomedical applications, where surfaces can be engineered to control cell attachment [45,46,47] and growth [48]. In [46] arrays of silicon pillars of various diameters and spacing were formed on a smooth silicon surface to study the preference for astroglial cell attachment. It was found that roughly 70% of the cells preferred to attach to the pillars over the etched regions. An example of this attachment can be seen in Figure 2.6, which has pillars 1 μm diameter with a spacing of 3.5 μm. A similar preference for adhesion of neural cells to microstructured over flat metal surfaces was found in [49].
2.2.3. Structures for surface-enhanced Raman spectroscopy (SERS)

Raman spectroscopy is a widely used technique to characterize various materials. A Raman spectroscopy measures the intensity of light that is inelastically scattered from a sample. Since Raman scattering is an inherently weak process, it is difficult to characterize certain types or small quantities of materials. These limitations have driven research into ways of enhancing Raman scattering. It was discovered that metal nanoparticles placed near the sample material can cause such enhancement, as a result of the excitation of surface plasmons [50]. Tip-enhancement has been accomplished by coating scanning probe microscopy tips in gold or silver, resulting in a 3 - 6 order of magnitude enhancement of Raman scattering [51]. An array of metal (or metal coated) nano-tips can also be used to create surface enhancing structures, allowing for even greater enhancement. It has been shown that surface-enhanced Raman spectroscopy (SERS) is capable of producing enhancement factors of up to $10^{14}$ making it possible to detect single molecules [52]. The amount of enhancement depends on many factors, but is based on field enhancement so a smaller radius of curvature will provide greater enhancement.

SERS is a surface sensitive technique which results in the enhancement of Raman scattering by molecules adsorbed on rough metal surfaces. The enhancement factor can be $10^{14}$-$10^{15}$, which allows the technique to be sensitive enough to detect single molecules [53]. So, by single pulse irradiation on the metal films sharp protrusions or nano-tips are made which will be easier to remove single molecules at the tip of the structure formed.
2.2.4. Physical and Electrical Probes

Nano-tips can be used as physical and electrical probes/contacts with very high spatial resolution; examples of devices using such tips are given in the following section and include: MEMS-based phase-change memory and MEMS-based thermoplastic memory devices, as well as scanning probe microscopy techniques.

2.2.5. Scanning Probe Microscopy

Nano-tips can also be used as physical probes to characterize materials by physically interacting with the surface. Atomic force microscopy (AFM) is a widely used example of this technique in which a very sharp tip on the end of a cantilever. The tip is placed in contact with a sample and used to physically scan the surface. While scanning, the deflection of the cantilever is measured using a laser and translated into a height measurement.

Since a single tip is used in nearly all scanning probe microscopy applications, the cost of the tip is often a secondary concern to its shape. Therefore, these techniques may not benefit a lot from a low-cost laser-based formation method. However, it is possible that future low-cost and/or portable microscopy techniques may be developed that require large numbers of physical or electrical probes. These future systems, possibly sensor-based applications, would benefit from a low-cost fabrication technique.
Chapter 3

Experimental Methods and Techniques, and Equipment

A Q-switched Nd:YAG laser (Powerlite 8010 from continuum Laser, Inc) capable of emitting 8 ns pulses with an energy up to 200mJ at 266 nm (4th harmonic) was used in this work. A diffraction limited lens was used in a demagnifying projection geometry to image individual, or small arrays of, pinholes onto the metal film, in order to produce circular spots of almost uniform intensity. The metal films of different thickness, were deposited on borosilicate glass (BSG) by a sputtering technique. The deposition of the films was done with RF magnetron sputtering, 100W RF power, 10mTorr Ar pressure and no substrate heating. The substrate used for the deposition of the films are borosilicate glass (BSG) and Si. The films were irradiated under low vacuum conditions (15mTorr) at fluence levels between 0.05-1.7 J/cm². The resulting structures were imaged by scanning electron microscopy (SEM), on a Phillips XL30 field-emission-gun scanning electron microscope.

The three main fabrication and characterization steps relevant to this research topic are:
3.1 Deposition of the films by RF or DC sputtering.

3.2 Formation of sharp protrusions and micro bumps using pulsed laser irradiation.

3.3 Characterization by scanning probe microscopy technique, scanning electron microscopy (SEM).

3.1 Deposition of the metal films by RF or DC sputtering system

The metal films were deposited by RF magnetron sputtering (in a Torr International customized deposition system) at a typical RF power of 100W, and deposition Ar gas pressure of 10mTorr usually with no substrate heating. The substrate material in most of the cases was borosilicate glass (BSG). A 3 inch diameter target was used in a balanced magnetron gun. The substrates were mounted on a rotating holder at a distance of 10cm from the target in sputter-up geometry. The substrate temperature could be controlled up to 400°C. All films were sputtered at a required RF power. To eliminate any contaminants from the target, a presputtering step was performed. The required thickness and the deposition rate was monitored by a quartz oscillator.

The sputtering system consists of a non magnetic, stainless steel vacuum chamber with a vacuum system including a turbo-molecular pump and a roughing pump. This system also includes a quartz crystal thickness monitor, one DC power supply, one RF power supply, a thickness monitor and controller, one RF 2” magnetron sputtering gun, one DC 3” magnetron sputtering gun and a motorized and heated substrate stage.

System Components:

Process chamber:
The chamber is made of non-magnetic 304 stainless steel and features a 4” viewing window and fully-opening front door for convenient substrate and source loading/unloading as well as easy chamber cleaning and maintenance. The dimensions of this chamber are 16” x 16” x 24”. The chamber carries the roughing valve, turbo pump, vacuum gauge, vent, two sputtering guns, two water-cooling feedthroughs for the thickness sensor sources and process gas inlets. The top plate carries the substrate holder with motor as well as the substrate heater.

**Vacuum Pumping System:**

This consists of a 300l/s molecular pump that has been mounted sideways backed by a matching dry mechanical pump with a foreline valve. A base vacuum of $10^{-7}$ Torr is guaranteed after a few precondition runs with dry N2. An operating vacuum of a few times $10^{-6}$ Torr can be achieved in about thirty minutes. The majority of the vacuum seals are of a conflate type with OFHC copper gaskets to help ensure the level of vacuum desired.

**RF Power Supply:**

This system utilizes a 300 Watt RF power supply with an automatic matching network.

**DC Power Supply:**

The 600 Watt DC supply uses solid state high frequency switching technology above 20 KHz. This power supply has an efficiency of 85% which is two times better than 60Hz tube bases power supplies.

**Magnetron Sputtering Guns:**
The 3” diameter gun is rated for up to 600 watts DC power and a 2” diameter gun rated at up to 300 Watts RF power.

**Thickness Monitor and Controller:**

The FTM-2000 deposition controller uses a quartz crystal thickness sensor and oscillator cables to measure film thickness and deposition rates. This can be used to enable/disable the power supplies based on final thickness or final time in order to provide a semi-automatic deposition process.

### 3.2 Laser Irradiation set up

The type of pulsed laser used in this project is Nd:YAG laser.

**Nd:YAG:**

Neodymium-doped yttrium aluminum garnet (Nd:Y$_3$Al$_5$O$_{12}$) is a crystal that is used as a lasing medium for solid-state lasers. The dopant, triply ionized neodymium, typically replaces yttrium in the crystal structure of the yttrium aluminum garnet, since they are of similar size. Generally the crystalline host is doped with around 1% neodymium by weight.

**Properties of Nd:YAG**

Nd:YAG is a four-level gain medium (except for the 946-nm transition as discussed below), offering substantial laser gain even for moderate excitation levels and pump intensities. The gain bandwidth is relatively small, but this allows for a high gain efficiency and thus low threshold pump power. Nd:YAG lasers can be diode pumped or lamp pumped. The type of pump source used here is flashlamp or laser diode.
The most common Nd:YAG emission wavelength is 1064 nm. Starting with that wavelength, outputs at 532, 355 and 266 nm can be generated by frequency doubling, frequency tripling and frequency quadrupling, respectively. Other emission lines are at 946, 1123, 1319, 1338 and 1444 nm. When used at the 946-nm transition, Nd: YAG is a quasi-three-level gain medium, requiring significantly higher pump intensities.

Nd:YAG is usually used in monocrystalline form, fabricated with the Czochralski growth method, but there is also ceramic (polycrystalline) Nd:YAG available in high quality and in large sizes. For both monocrystalline and ceramic Nd:YAG, absorption and scattering losses within the length of a laser crystal are normally negligible, even for relatively long crystals.

A Q-switched Nd: YAG laser (Powerlite 8010 from Continuum Laser, Inc) capable of emitting 8 ns pulses with an energy up to 200mJ at 266 nm (4th harmonic) is used in this work.

To produce circular irradiation spots which are of uniform intensity on the sample surface, a projection technique with a demagnifying geometry was used in conjunction with a diffraction-limited lens to image individual or small arrays of pinholes. Below is the schematic block diagram of the experimental laser setup used in this research.
The fluence level can be adjusted by means of a polarizing attenuator. This attenuator consists of a half-wave plate and a polarizing beam splitter. As the laser pulse passes through the half-wave plate, it alters the beams polarization according to the rotation angle. The output from this half-wave plate is then passed through a polarizing cube, thereby separating the laser pulse into two parts based on its polarization. A portion of the beam continues through the setup while the remaining beam is discarded by means of a beam dump.

The output of the laser has a Gaussian spatial distribution; therefore, to ensure a uniform intensity within the irradiated spot, the beam is expanded through the use of a telescope. This telescope consists of two lenses and expands the beam by a factor of four which can be changed if needed by using other lens combinations. A mask containing an individual or small array of circular pinholes is placed in the center of this expanded beam; allowing a small and relatively uniform section from the center of the expanded beam to be used for sample irradiation. The individual or small arrays of pinholes within
the mask are then demagnified by a factor of ten via a diffraction-limited lens. This demagnification increases the fluence level to the required intensity as well as allowing the use of mask with more practically-sized hole patterns (i.e. micrometer-sized holes would be difficult and expensive to make, and size variations would be even more significant).

Finally, the beam passes through the quartz window of a hermetic irradiation chamber before being focused the onto sample surface. This chamber is used to examine the effects of the gas atmosphere on the formation of these structures. The chamber itself is mounted onto a high-precision XYZ-stage providing focus control as well as sample positioning.

Figure 3.2.2: The experimental laser irradiation setup, the inset figure shows a close-up of the irradiation chamber.
3.3 Characterization by scanning electron microscopy (SEM)

3.3.1 Scanning Electron Microscopy (SEM)

SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

Scanning electron microscopy (SEM) is one of the most versatile and well known analytical techniques. Compared to conventional optical microscope, an electron microscope offers advantages including higher magnification, large depth of focus, great resolution and ease of sample preparation and observation. Electrons generated from an electron gun enter a surface of a sample and generate low energy secondary electrons. The intensity of these secondary electrons is governed by the surface topography of the sample as well as by the type of material. An image of the sample surface is therefore constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam [54,55].
A detailed explanation of how a typical SEM functions follows:

1. The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons.

2. The stream is condensed by the first condenser lens (usually controlled by the "coarse probe current knob"). This lens is used to both form the beam and limit the amount of current in the beam. It works in conjunction with the condenser aperture to eliminate the high-angle electrons from the beam.

3. The beam is then constricted by the condenser aperture (usually not user selectable), eliminating some high-angle electrons.

4. The second condenser lens forms the electrons into a thin, tight, coherent beam and is usually controlled by the "fine probe current knob".

5. A user selectable objective aperture further eliminates high-angle electrons from the beam.

6. A set of coils then "scan" or "sweep" the beam in a grid fashion (like a television),
dwelling on points for a period of time determined by the scan speed (usually in the microsecond range)

7 The final lens, the Objective, focuses the scanning beam onto the part of the specimen desired.

8 When the beam strikes the sample (and dwells for a few microseconds) interactions occur inside the sample and are detected with various instruments

9 Before the beam moves to its next dwell point these instruments count the number of interactions and display a pixel on a CRT whose intensity is determined by this number (the more reactions the brighter the pixel).

10 This process is repeated until the grid scan is finished and then repeated, the entire pattern can be scanned 30 times per second [56].

Figure 3.3.1.2: Schematic diagram of SEM functions

3.3.2 Optical Microscopy

Optical microscopy is a type of microscopy wherein it uses visible light and a system of lenses to magnify images of small samples. Optical microscopes can be very simple, although there are many complex designs which aim to improve resolution and
sample contrast. Scanning electron microscopy is an alternate to optical microscopy which do not use visible light to magnify images [57]. Optical microscopy is used extensively in microelectronics, nanophysics, biotechnology, pharmaceutics research and microbiology [57]. In order to overcome the limitations set by the diffraction limit of visible light other microscopes like (SEM, AFM) have been designed which use other waves. There are two basic configurations of the conventional optical microscope, the simple (one lens) and compound (many lenses). The vast majority of modern research microscopes are compound microscopes while some cheaper commercial digital microscopes are simple single lens microscopes.

Figure 3.3.3.1: The optical microscope used in this project: Olympus BX51 with BF/DF/polarization capabilities and digital camera.
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<th>Materials</th>
<th>Heat capacity(C) in [J/(Kg*k)]</th>
<th>Youngs modulus(E) in $10^9$[Pa]</th>
<th>Thermal conductivity(K) in [w/(m*K)]</th>
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</table>

Table 1: Relevant material properties[59]
Chapter 4

Results and Discussion

This chapter describes and discusses the results obtained from the single-pulse laser irradiation of thin metal films. This work mainly focuses on irradiation of copper films, with the resulting structures and formation dependences described in detail. Other metal films including gold, aluminum and titanium were also examined in an effort to better understand the material parameters that influence the formation mechanism.

4.1 Irradiation of Gold Films

Conditions for the fabrication of various sharp protrusions and bump-like structures upon irradiation of Au films on borosilicate glass (BSG) substrates have been identified and are reported by our group in [22]. Figure [4.1.1] shows an SEM image of the microstructures obtained as a result of single-pulse laser irradiation of a 300 nm-thick gold film on BSG at a fluence of 0.66 J/cm² under low-vacuum conditions using spot sizes of 3 μm. As seen in this figure, the resulting structures contain protrusions that are 2 to 3 μm in height and have nano-scale sharpness.
Figure 4.1.1: An SEM image of an array of sharp structures formed on a 300 nm gold film with a borosilicate glass (BSG) substrate [22].

Figure [4.1.2] (a) shows result for irradiation of Au films at low fluence level of 0.24 J/cm², in which only small bumps with very small protrusions develop. At medium fluence levels of 0.44 J/cm², Figure [4.1.2] (b) reveals an increase in the size of both the protrusion and underlying bump. This type of structures are distinguished by the vertical shaft beginning to narrow, forming a droplet at the apex. Figure [4.1.2] (c) is at elevated fluence levels of 0.6 J/cm², and is characterized by the complete removal of the attached droplet. Within this range, it is possible to reliably form sharp protrusions. The height and shape dependences on the fluence in this range are complex, though predictable and reproducible. Initially, the height of the protrusions increase, then, at higher fluence levels, it actually decreases with the volume of the underlying bump significantly increasing. Figure [4.1.2] (d), produced at even higher fluence levels greater than 1.0 J/cm², results in less uniform shapes as well as tilted protrusions. Further increases in the fluence result in the formation of craters and ablation holes.
Formation Mechanism:

Formation of such structures was studied on both silicon and BSG substrates [22]. The obtained results for the 300 nm films indicate the substrate has a significant effect on the type of modification that occurs within the film. Most generally, the lower thermal conductivity of the BSG substrate leads to a more non-uniform temperature profile within the irradiated spot: the central part of the spot remains at a much higher temperature than the periphery for a significant amount of time. The shape changed from a small bumps with very small protrusions, to a small bump with increased protrusions, to a sharp protrusion on a bump, and finally to a tilted protrusions, with the increase in laser fluence.
levels. The mechanism of formation of these structures is rather complex, and not well understood. Our group’s previous results indicate that there is a complex interplay of rapid melting and solidification and related surface tension effects, combined with thermoplastic deformation (and possibly pressure build-up, responsible for the formation of the hollow underlying bump), and the formation of a viscous flow vertical nano-jet which is pinched off by an apical droplet (with or without its detachment) [22, 60].

Below are presented SEM data on laser micro-structuring of films using single-pulse localized laser irradiation on thin gold films (300 nm) with 2.5μm spot size and on thick gold films (600 nm and 650 nm), which complements the earlier work on gold films irradiation.

Figures [4.1.3][4.1.4][4.1.5] present SEM images of microstructures on Au with BSG substrates obtained as a result of single-pulse laser irradiation of gold films at different fluence level under low vacuum conditions. Any minor differences in the size of these microstructures obtained at a fixed fluence and spot size are due to slight variations in the mask pinhole size and shape (i.e., mask imperfections). Overall, we observe a consistent dependence on fluence and spot size, which, in principle, can be used to control the formation process. Even better control could be achieved upon improving the pinholes shape and size uniformity.

Figures [4.1.3] present SEM images of the microstructures obtained as a result of single-pulse laser irradiation of a 300 nm-thick gold film with a thick Ti underlayer (~100nm) on BSG at a higher fluence level 1.7 J/cm$^2$ and 2.1 J/cm$^2$ under low-vacuum conditions using spot sizes of 2.5 μm. Figure [4.1.3] (a) shows results at fluence levels 1.69 J/cm$^2$ where donut shaped ring sitting in the depression is formed. Figure [4.1.3] (b)
shows results at fluence levels 2.049 J/cm$^2$ where donut shaped ring is formed which is wider.

Figure 4.1.3: SEM images of bumps formed on a 300 nm-thick gold film with a thick Ti underlayer on a BSG substrate irradiated at various fluence levels showing the different development regimes

Figures [4.1.4] present SEM images of the microstructures obtained as a result of single-pulse laser irradiation of a 600 nm-thick gold film with a thick Ti underlayer on BSG at a higher fluence levels 1.5 J/cm$^2$ under low-vacuum conditions using spot sizes of 2.5 μm. Figure [4.1.4] (a) shows results at fluence levels 1.53 J/cm$^2$ where donut shaped ring sitting in the depression is formed.
Discussion: Similar results were observed upon irradiation of the 300 and 600 nm films, the results of which can be seen in Figure [4.1.3] and Figure [4.1.4]. As seen, nearly identical structures form within the various thicknesses of the examined films. No bumps or sharp protrusions form on this type of films, with thick Ti underlayer. The Ti underlayer provides extremely good adhesion and its significant thickness, combined with very different thermal properties—lower heat conductivity and higher melting point—apparently entirely alters the mechanism of formation of the structures described earlier.

Figures [4.1.5] present SEM images of the microstructures obtained as a result of single-pulse laser irradiation of a 650 nm-thick gold film on BSG (with a very thin Ti adhesion layer just as in the earlier experiments performed by our group) fluence levels 0.4 J/cm², 0.5 J/cm², 0.6 J/cm², 0.8 J/cm², 1.0 J/cm², 1.2 J/cm² under low-vacuum conditions using spot sizes of 2.5 μm. As seen in this figure, the resulting structures are 2 to 3 μm in height and have nano-scale sharpness. Figure [4.1.5] (a) shows the results at fluence levels 0.4 J/cm² where only small bumps with small protrusions develop. Figure [4.1.5] (b) shows the results at fluence levels 0.5 J/cm² where there is an increase in the
size of the protrusion and the underlying bump, droplets are formed at the end of the protrusion. Figure [4.1.5] (c) shows the results at fluence levels 0.6 J/cm² where most of the structures in this array consist of vertical shafts with the droplets fully detached and removed from the area under the *low-vacuum* conditions. Figure [4.1.5] (d) shows the results at fluence levels 0.8 J/cm² where all the droplets are removed and there are sharp protrusions like those seen in the figure. Figure [4.1.5] (e) shows the results at the fluence levels 1.0 J/cm² where tips are formed. Figure [4.1.5] (f) shows the results at the fluence levels 1.2 J/cm², results in the formation of craters and ablation holes.
Figure 4.1.5: SEM images of bumps formed on a 650 nm-thick gold film with a BSG substrate irradiated with a 2.5 μm spot at different fluence levels.

**Discussion:** It is clear from Figure [4.1.4] that there is a significant difference between the structures under different fluence levels. At lower fluence level it forms small bumps with small protrusions and goes onto form craters and ablation holes at high fluence level of 1.2J/cm². These results are similar to those obtained earlier by our group. Very similar structures form, with similar dependence on the fluence level, as well as a comparable range of parameters space within which a controllable and reproducible formation of uniformly shaped structures is possible.

### 4.2 Irradiation of Copper Films

Single-pulse localized irradiation of copper films experiments comprise the main part of this thesis research project, and the results obtained represent the most important findings of our work. The results below present SEM images of microstructures formed on a wide range of thicknesses (250 nm, 500nm, 750nm, 1500nm) of thick copper films on borosilicate glass (BSG). This includes a 500nm thick copper film deposited at an increased temperature of 200°C on a BSG substrate (in order to examine the effect of the different film morphology, grain size etc.) and a 500nm thick copper film on a Si substrate (to examine the role of the substrate materials, and specifically the very different thermal conductivity). The structures were obtained as a result of single-pulse laser irradiation for different thickness at different fluence level under mostly low vacuum conditions, but we also performed experiments in laboratory air environment.
CASE 1: In this case we present SEM images of films after irradiation with a single pulse, and irradiation spot diameter of 2.5 μm for different film thicknesses. Here we follow the structures that form as a function of the fluence level at each thickness level.

Figure 4.2.1: SEM images of a 250 nm thick copper film with a BSG substrate irradiated with a 2.5 μm spot at different fluence levels.

(b) 250nm Cu on BSG, 0.8J/cm² 

(c) 250nm Cu on BSG, 1.2J/cm² 

Figures [4.2.1] present SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 250 nm-thick copper film on BSG at fluence levels 0.4
J/cm$^2$, 0.8 J/cm$^2$, 1.2 J/cm$^2$. Figure [4.2.1] (a) is at a fluence level of 0.4 J/cm$^2$ where only small bumps with small protrusions develop. Figure [4.2.1] (b) is at a fluence levels 0.8 J/cm$^2$ where there is an increase in the size of the protrusion and the underlying bump. Figure [4.2.1] (c) is at a fluence level of 1.2 J/cm$^2$ which results in the formation of a similar protrusion sitting in a depression, but with larger underlying bump.

**Discussion:** It is seen that a round-top, wide protrusion (or a bump) forms in the center of a depression, and upon increasing the fluence level, the protrusion grows in height and the depression widens in a controllable way.

Figures [4.2.2] present SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 500 nm-thick copper film on BSG fluence level 0.4 J/cm$^2$, 0.45 J/cm$^2$, 0.7 J/cm$^2$. As seen in this figure, the resulting structures are 2 to 3μm in height and can have nano-scale sharpness on top. Droplets are often formed at the top of the protrusion. Figure [4.2.2] (a) is at a fluence level of 0.4 J/cm$^2$ where only small bumps with small protrusions develop. Figure [4.2.2] (b) is at a fluence level of 0.45 J/cm$^2$ where there is an increase in the size of the protrusion droplets are formed at the end of the protrusion in both (a) and (b). Figure [4.2.2] (c) is at a fluence level of 0.7 J/cm$^2$ where there is an increase in the size of the protrusion and the underlying bump, and the protrusions are not as thin and sharp on top.
Figure 4.2.2: SEM images of a 500 nm-thin copper film with a BSG substrate irradiated with a 2.5 μm spot at different fluence levels.

(a) 500nm Cu on BSG, 0.4J/cm²  500nm Cu on BSG, 0.4J/cm²

(b) 500nm Cu on BSG, 0.45J/cm²  500nm Cu on BSG, 0.45J/cm²

(c) 500nm Cu on BSG, 0.7J/cm²  500nm Cu on BSG, 0.7J/cm²
**Discussion:** Most of the structures in Figure [4.2.2] have droplets at the end of the apex. The resulting structures in the case of 500nm-thick films are generally much sharper, but somewhat less controllable than those obtained in the 250nm case. With the increase in the fluence levels the development of a large and slanted protrusion which contains a large droplet at the tip is observed.

Figures [4.2.3] present SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 500 nm-thick copper film on a BSG substrate, deposited at an increase in the substrate temperature of $200^\circ$ C which resulted in a somewhat smoother film with no cracks as compared to the 500nm-thick film in Figure [4.2.3] the film was irradiated at higher fluence levels of 0.7 J/cm$^2$, or 0.9 J/cm$^2$ under low vacuum conditions using spot sizes of 2.5 μm. Figure [4.2.3] (a) is at a fluence level of 0.7 J/cm$^2$ where only small bumps with small protrusions develop. Figure [4.2.3] (b) is at a fluence level of 0.9 J/cm$^2$ where there is small increase in the protrusion and the underlying the bump.
Figure 4.2.3: SEM images of a 500 nm-thick copper film with a BSG substrate irradiated with a 2.5 μm spot and at increased temperature of 200°C at different fluence levels.

Discussion: In Figure [4.2.3] the protrusions are smaller, wider, and sit on larger underlying bumps. As the fluence increases there is not much change in the size of the protrusion, but we see an increase in the bump size. It can be seen that the structures in Fig. 4.2.3a and Fig. 4.2.2c are substantially different inspite of being obtained the same fluence, spot size, and the same film thickness. This is probably due to the fact that the films deposited at 200°C is smoother with fewer cracks and therefore a larger area has been directly melted by the laser pulse. We have clear indications that the underlying bumps in Fig. 4.2.3 are actually hollow in nature, similarly to what was consistently observed in the case of gold films.
Figures [4.2.4] present SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 750 nm-thick copper film on BSG at fluence levels 0.4 J/cm², 0.5 J/cm², 0.9 J/cm², 1.0 J/cm² under low-vacuum conditions using spot sizes of 7.5 μm. Figure [4.2.4] (a) is at a fluence level of 0.4 J/cm² where only small bumps with a small surrounding area of re-solidified material develop. Figure [4.2.4] (b) is at a fluence level of 0.5 J/cm² where the structures increase in height and begin to narrow and pinch-off. Figure [4.2.4] (c) is at a fluence level of 0.9 J/cm² where there is an increase in the size of the protrusion and the underlying bump. Figure [4.2.4] (d) is at a fluence level of 1.0 J/cm² where ablations craters begin to develop.

Figure 4.2.4: SEM images of a 750 nm-thick copper film with a BSG substrate irradiated with a 7.5 μm spot at different fluence levels.
Discussion: In this set of experiments done by systematically increasing the fluence, when compared to the previous sets, we changed not only the film thickness to 750nm, but also the irradiation spot size from 2.5 μm to 7.5 μm. In Figures [4.2.4] the formation begins as small bumps with a small surrounding area of re-solidified material to craters when there is an increase in the fluence level and this is at spot size 7.5 μm. For 750nm and 1500nm thick copper films, we could not obtain any significant changes upon irradiation with a spot size of 2.5 μm – the films were too thick and required much higher fluence in order to overcome the lateral heat loss through the increased thickness of the film. Considering the high film thickness, the irradiation with smaller spot sizes (i.e., 2.5 μm, 5.0 μm) does not produce observable changes even at relatively high fluence levels.

CASE 2: In this case we present SEM images of microstructures obtained as a result of single-pulse laser irradiation of a copper film on a BSG substrate, deposited at a higher substrate temperature of 200°C, which resulted in a somewhat smoother film with no cracks as compared to the 500nm-thick deposited at room temperature. Four spot sizes were used (i.e. 2.5μm, 5.0μm, 7.5μm, 10.0μm) and the effect of the spot size is of main interest in this case.

Figures [4.2.5] include SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 500 nm-thick copper film on BSG under low-vacuum conditions using spot sizes of 2.5μm and at increased temperature of 200°C. Figure [4.2.5] (a) is at a fluence level of 0.8 J/cm² results in the formation of small bumps with small protrusions.
Figure 4.2.5: SEM images of a 500 nm-thick copper film with a BSG substrate irradiated with a 2.5 μm spot at different fluence levels.

Figures [4.2.6] include SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 500 nm-thick copper film on BSG at fluence levels of 0.4 J/cm$^2$, 0.6 J/cm$^2$, 0.8 J/cm$^2$, and 0.9 J/cm$^2$ under low-vacuum conditions using spot sizes of 5.0μm and at increased temperature of 200$^\circ$C. Figure [4.2.6] (a) is at a fluence level of 0.4 J/cm$^2$ and results in the formation of small bumps in the depression. Figure [4.2.6] (b) is at a fluence level of 0.6 J/cm$^2$ and results in the formation of small bumps with very small protrusions in the middle of a circular depression. Figure [4.2.6] (c) shows results at 0.8J/cm$^2$ where there is an increase in the size of the protrusion although the underlying bump does not increase significantly. Figure [4.2.6] (d) shows results at 0.9 J/cm$^2$ where craters and holes are formed.
Figure 4.2.6: SEM images of a 500 nm-thick copper film with a BSG substrate irradiated with a 5.0 μm spot at different fluence levels.

Figures [4.2.7] include SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 500 nm-thick copper film on BSG at fluence levels 0.2 J/cm², 0.4 J/cm² under low-vacuum conditions using spot sizes of 7.5μm and at increased temperature of 200°C. Figure [4.2.7] (a) is at a fluence level of 0.2 J/cm² where small bumps are formed with very small protrusions. Figure [4.2.7] (b) is at a fluence level of 0.4 J/cm² where majority formed are bumps.
Figure 4.2.7: SEM images of a 500 nm-thick copper film with a BSG substrate irradiated with a 7.5 μm spot at different fluence levels.

Figures [4.2.8] include SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 500 nm-thick copper film on BSG at fluence levels of 0.3 J/cm² or 0.4 J/cm² under low-vacuum conditions using spot sizes of 10.0μm and at increased temperature of 200°C. Figure [4.2.8] (a) is at a fluence level of 0.2 J/cm² where small bumps are formed with very increase in the size of the protrusions. Figure [4.2.8] (b) shows results at 0.4 J/cm² which produces holes.
Case 2 is a systematic study of the irradiation of 500 nm thick copper film which was deposited at increased temperature of 200°C and irradiated at different spot sizes (i.e. 2.5μm, 5.0μm, 7.5μm, 10.0μm). At spot size 2.5μm the size of the protrusion underlying the bump is small and varies little at all studies fluence levels. But as we increase the spot size to 5.0μm large protrusions with large droplet at the end of the apex are formed. As the fluence level is further increased at the same spot size of 5.0μm holes are formed in the structure, revealing a hollow nature. In the case of 7.5μm and 10.0μm spot sizes, only within a narrow fluence range, at low fluence levels, large protrusions
with large droplet at the end of the apex are formed. At higher fluence levels, eventually holes and craters in the hollow structures are obtained.

**CASE 3:**

In this case we present images obtained as a result of single pulse laser irradiation on 500nm thick copper film (deposited at room temperature, i.e. with micro-cracks morphology) on a BSG substrate at 2.5μm, 5.0μm, 7.5μm spot sizes. Again, the dependence on the spot size is of interest in this case.

Figures [4.2.9] include SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 500 nm-thick copper film on BSG at fluence levels of 0.5 J/cm$^2$ and 0.7 J/cm$^2$ under low-vacuum conditions using spot sizes of 2.5μm. Figure [4.2.9] (a) is at a fluence level of 0.5 J/cm$^2$ where small bumps are formed with very small protrusions. Figure [4.2.9] (b) shows results at 0.7 J/cm$^2$ where there is an increase in the size of the protrusion with the increase in the bump size and droplets at the end of the apex.
Figure 4.2.9: SEM images of a 500 nm-thick copper film with a BSG substrate irradiated with a 2.5 μm spot at different fluence levels.

Figures [4.2.10] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 500 nm-thick copper film on BSG at fluence levels of 0.2 J/cm² and 0.23J/cm² under low-vacuum conditions using spot sizes of 5.0μm. Figure [4.2.10] (a) is at a fluence level of 0.2 J/cm² where small bumps are formed with very small protrusions. Figure [4.2.10] (b) shows results at 0.23 J/cm² where there is an increase in the size of the protrusion with the increase in the bump size and droplets at the end of the apex.
Figure 4.2.10: SEM images of a 500 nm-thick copper film with a BSG substrate irradiated with a 5.0 μm spot at different fluence levels.

(a) 500nm Cu on BSG, 0.2J/cm²

(b) 500nm Cu on BSG, 0.23J/cm²

500nm Cu on BSG, 0.23J/cm²

Figures [4.2.11] includes SEM images of microstructures obtained as the result of single-pulse laser irradiation of a 500 nm-thick copper film on BSG at fluence level 0.2J/cm² under low-vacuum conditions using spot sizes of 7.5μm. Figure [4.2.11] (a) is at fluence levels 0.2 J/cm² where craters and holes are formed.
Figure 4.2.11: SEM images of a 500 nm-thick copper film with a BSG substrate irradiated with a 7.5 μm spot at 0.2 J/cm² fluence.

Discussion: Case 3 is a study of the irradiation of the 500nm thick copper film at different spot sizes (i.e. 2.5μm, 5.0μm, 7.5μm). At spot size 2.5μm the size of the protrusion underlying the bump is small and as we increase the fluence level droplets are formed at the end of the apex where as in case 2 the size of the protrusion underlying the bump is small and varies little at all studies fluence levels. As the spot size is increased to 5.0μm droplets at the end of the apex started forming from lower fluence levels which is similar to case 2. And as we further increase the spot size to 7.5μm craters and holes are formed at low fluence levels. In case 2 of 7.5μm and 10.0μm spot sizes, only within a narrow fluence range, at low fluence levels, large protrusions with large droplet at the end of the apex are formed. At higher fluence levels, eventually holes and craters in the hollow structures are obtained.
CASE 4:

In this case we compare the images of structures, obtained as a result of single pulse laser irradiation of 250nm thick copper film on a BSG substrate in air or vacuum. The irradiation spot diameters used are 2.5μm, 5.0μm, 7.5μm, and 10.0μm.

Figures [4.2.12] include SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 250 nm-thick copper film on BSG at a fluence of 0.5J/cm² under air and low-vacuum conditions using spot sizes of 2.5μm. Figure [4.2.12] (a) is at a fluence of 0.5J/cm² under air where there is lot of disturbance on the substrate due to air. Figure [4.2.12] (b) shows results where small bumps and small protrusions in the depression are formed under low vacuum conditions.

![SEM images of microstructures](image)

(a) 250nm Cu on BSG, 0.5J/cm² in air  
(b) 250nm Cu on BSG, 0.5J/cm² in vacuum

Figure 4.2.12: SEM images of a 250 nm-thick copper film with a BSG substrate irradiated with a 2.5 μm spot at 0.5J/cm² fluence in both air and low vacuum conditions.

Figures [4.2.13] include SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 250 nm-thick copper film on BSG at fluence of 0.45J/cm² under air and low-vacuum conditions using spot sizes of 5.0μm. Figure [4.2.13] (a) is at fluence 0.45J/cm² under air where there is lot of disturbance on the substrate due
to air. Figure [4.2.13] (b) shows results where small bumps in the depression are formed under low vacuum conditions.

Figure 4.2.13: SEM images of a 250 nm-thick copper film with a BSG substrate irradiated with a 5.0 \( \mu \text{m} \) spot at 0.45 J/cm\(^2\) fluence in both air and low vacuum conditions.

(a) 250nm Cu on BSG, 0.45J/cm\(^2\) in air  (b) 250nm Cu on BSG, 0.45J/cm\(^2\) in vacuum

Figures [4.2.14] include SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 250 nm-thick copper film on BSG at a fluence of 0.6 J/cm\(^2\) under air and low-vacuum conditions using spot sizes of 7.5 \( \mu \text{m} \). Figure [4.2.14] (a) is at a fluence of 0.6 J/cm\(^2\) under air where there is lot of disturbance on the substrate due to air. Figure [4.2.14] (b) shows results where holes are formed under low vacuum conditions.
Figure 4.2.14: SEM images of a 250 nm-thick copper film with a BSG substrate irradiated with a 7.5 μm spot at 0.6J/cm² fluence in both air and low vacuum conditions.

Figures [4.2.15] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 250 nm-thick copper film on BSG at fluence of 0.6J/cm² under air and low-vacuum conditions using spot sizes of 10.0μm. Figure [4.2.15] (a) is at fluence of 0.6J/cm² under air where roughened spots with irregular fine fiber-like material, of unknown origin, probably due to a reaction with the atmospheric air are observed on the substrate. Figure [4.2.15] (b) is at 0.6J/cm² fluence levels where craters and holes are formed under low vacuum conditions.
Discussion: Case 4 reveals the role of the gas environment upon this laser irradiation processing. When laser irradiation is done under air the roughened spots with irregular fine fiber-like material, of unknown origin, probably due to a reaction with the atmospheric air is observed and the structures formed on the surface of the substrate are not seen. But when the same irradiation is done under vacuum the structures that are formed are much smoother, less irregular and more reproducible.

CASE 5:

In this case we present the images of microstructures obtained as a result of single pulse laser irradiation of very thick copper films (1500nm thick) on a BSG substrate irradiated using 7.5μm, or 10.0μm spot sizes at different fluence levels.

Figures [4.2.15] include SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 1500 nm copper film on BSG under low-vacuum conditions using spot sizes of 7.5μm. Figure [4.2.15] (a) is at a fluence of 0.5J/cm² where

(a) 250nm Cu on BSG, 0.6J/cm² in air
(b) 250nm Cu on BSG, 0.6J/cm² in vacuum

Figure 4.2.15: SEM images of a 250 nm-thick copper film with a BSG substrate irradiated with a 10.0 μm spot at 0.6J/cm² fluence in both air and low vacuum conditions.
irradiation of the film causing superheating, partial melting and ablation, but no formation of regular or predictable shape structures. Figure [4.2.15] (b) shows results at 1.0 J/cm² where similar results are seen with the addition of irregular-shape droplets forming on some spots.

Figure 4.2.15: SEM images of a 1500 nm-thick copper film with a BSG substrate irradiated with a 7.5 μm spot at different fluence levels.

Figures [4.2.16] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 1500 nm-thick copper film on BSG under low-vacuum conditions using spot sizes of 10.0μm. Figure [4.2.16] (a) is at fluence of 0.9J/cm² where
roughened spot surface is observed as a result of partial melting and ablations. Figure [4.2.16] (b) shows similar results at 1.4 J/cm² where the roughening of the surface is enhanced by the higher heat input.

![SEM images of a 1500 nm copper film with a BSG substrate irradiated with a 10.0 μm spot at different fluence levels.](image)

(a) 1500nm Cu on BSG, 0.9J/cm²  
(b) 1500nm Cu on BSG, 1.4J/cm²

Figure 4.2.16: SEM images of a 1500 nm copper film with a BSG substrate irradiated with a 10.0 μm spot at different fluence levels.

**Discussion:** In this case the irradiation was performed on very thick (i.e.almost bulk case) 1500nm thick copper film. It is seen that no formation of any regular shape structures could be obtained. Instead, the formation of roughened surface, due to melting and ablation is observed, together with large, irregular-shape droplets in some cases.
CASE 6:

In this case we present the images of microstructures obtained as a result of single pulse laser irradiation of 500nm thick copper film on a Si substrate irradiated with 5.0 μm, 7.5μm, and 10.0μm spot sizes at different fluence levels. The role of the substrate (i.e.BSG vs. Si) is of main interest in this case.

Figures [4.2.17] include SEM images the result of single-pulse laser irradiation of a 500 nm copper film on Si under low-vacuum conditions using spot sizes of 5.0μm. Figure [4.2.17] (a) is at a fluence level of 1.0J/cm² where a resolidified surface, smoother than the original surface, is observed. Figure [4.2.17] (b) shows results at 1.7 J/cm² where larger bumps are formed.

(a) 500nm Cu on Si 1.0 J/cm²  
(b) 500nm Cu on Si 1.7J/cm²

Figure 4.2.17: SEM images of a 500 nm copper film with a Si substrate irradiated with a 5.0 μm spot at different fluence levels.

Figures [4.2.18] include SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 500 nm copper film on Si under low-vacuum conditions using spot sizes of 7.5μm. Figure [4.2.18] (a) is at a fluence 1.0J/cm² where barely noticeable bumps are formed. Figure [4.2.18] (b) shows results at 1.7 J/cm² where a little better depressed bumps are seen.
Figure 4.2.18: SEM images of a 500 nm copper film with a Si substrate irradiated with a 7.5 μm spot at different fluence levels.

Figures [4.2.19] include SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 500 nm copper film on Si under low-vacuum conditions using spot sizes of 10.0μm. Figure [4.2.19] (a) is at fluence 1.0J/cm$^2$ where donut-like shapes, apparently due to significant melting of the film, are formed. Figure [4.2.19] (b) shows results at 1.7 J/cm$^2$ where similarly shaped but larger structures are observed, having a somewhat roughened interior.
Figure 4.2.19: SEM images of a 500 nm copper film with a Si substrate irradiated with a 10.0 μm spot at different fluence levels.

**Discussion:** Most of the structures in case (6) are minimally raised bumps except the structures formed when irradiated with 10.0μm spot size at relatively high fluence levels are donut shaped. The structures on copper film with a Si substrate where most of the structures are barely seen when irradiated with 5.0μm spot size at higher fluence level. When the film is irradiated with lower spot size of 2.5μm there is nothing seen on the substrate of the film inspite of irradiating with high fluence level. As the spot size is increased to 7.5μm and 10.0μm little better depressive bumps and donut-like shaped structures are observed at high fluence levels. But, in the case of copper film with a BSG substrate typically small bumps with very small protrusions are observed at lower spot size of 2.5μm and at lower fluence level. As the spot size is increased to 5.0μm small bumps with very small protrusions are replaced by forming structures which are increased in the bump size and droplets at the end of the apex. And when the substrate is irradiated with 7.5μm spot size craters and holes are formed.

### 4.3 Irradiation of Aluminum Films

Other metal films including aluminum and titanium were also examined in an effort to better understand the effects the film material properties have on the resulting structures and their formation.

Aluminum has the lowest melting point, among all metal films attempted in these laser irradiation studies, together with low viscosity and surface tension [See table 1]. In most of the cases aluminum microbumps with no protrusions are observed. Although in [58], a somewhat related method was shown to produce protrusions in aluminum films. A
systematic study of the aluminum film case therefore is needed to determine what type of microstructures, if any, can be obtained by single-pulse laser irradiation, and what level of controllability could be achieved.

**CASE 1:**

In this case we present SEM images of films after irradiation with a single pulse, 2.5 μm in diameter for different film thicknesses, *as a function of the fluence level.* Figures [4.3.1] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a *300 nm-thick* aluminum film on BSG under low-vacuum conditions using spot sizes of 2.5μm. Figure [4.3.1] (a) is at a fluence of 0.5J/cm² where mostly small bumps are seen. Figure [4.3.1] (b) is at a fluence of 0.9J/cm² where holes in a ring like, or donut-shaped, structures are formed.
Figure 4.3.1: SEM images of a 300 nm-thick aluminum film with a BSG substrate irradiated with a 2.5 μm spot at different fluence levels.

(a) 300nm Al on BSG, 0.5J/cm²
(b) 300nm Al on BSG, 0.9J/cm²

Figure 4.3.2 includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 400 nm-thick aluminum film on BSG under low-vacuum conditions using spot sizes of 2.5μm. Figure [4.3.2] (a) is at fluence level 0.9J/cm² where microbumps again are seen, but no central protrusions or droplets of any kind are observed. It is possible that the low surface tension of aluminum is the main reason for the drastic difference between the case of aluminum on one hand, and gold and copper on the other. The lower thermal conductivity of Al when compared to Au and Cu
most likely plays a role too. Figure [4.3.2] (b) showing the case at 1.0J/cm² reveals a small hole in the center of a microbump where a protrusion would be typically expected in Au or Cu films.

![Image](image.png)

(a) 400nm Al on BSG, 0.9J/cm²  (b) 400nm Al on BSG, 1.0J/cm²

Figure 4.3.2: SEM images of a 400 nm-thick aluminum film with a BSG substrate irradiated with a 2.5 μm spot at different fluence levels.

**CASE 2:**

In this case we present images of microstructures obtained as a result of single-pulse laser irradiation on 400nm thick aluminum film with a BSG substrate irradiated with 2.5μm, 5.0μm, 7.5μm spot sizes. The spot size dependence is of main interest here. Figures [4.3.3] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 400 nm-thick aluminum film on BSG under low-vacuum conditions using spot sizes of 2.5μm. Figure [4.3.3] (a) at a fluence level of 1.1J/cm² shows a small hole in the center of a microbump. Figure [4.3.3] (b) at 1.2J/cm² forms the same but with increase in the size of the microbump.
Figure 4.3.3: SEM images of a 400 nm-thick aluminum film with a BSG substrate irradiated with a 2.5 μm spot at different fluence levels.

Figures [4.3.4] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 400 nm-thick aluminum film on BSG under low-vacuum conditions using spot sizes of 5.0μm. Figure [4.3.4] (a) at fluence 0.5J/cm² results in the formation of small round bumps, Figure [4.3.4] (b) at 0.52J/cm² melting and ablations holes are formed in a ring like structure.
Figure 4.3.4: SEM images of a 400 nm-thick aluminum film with a BSG substrate irradiated with a 5.0 μm spot at different fluence levels.

Figures [4.3.5] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 400 nm-thick aluminum film on BSG under low-vacuum conditions using spot sizes of 7.5μm. Figure [4.3.5] (a) is at a fluence of 0.25J/cm² results in the formation of small round bumps, Figure [4.3.5] (b) at 0.3J/cm² holes and, in many cases, larger-size bumps are formed.

Figure 4.3.5: SEM images of a 400 nm-thick aluminum film with a BSG substrate irradiated with a 7.5 μm spot at different fluence levels.
CASE 3:

In this case we present images of microstructures obtained as a result of single-pulse laser irradiation on 300nm thick aluminum film with a BSG substrate irradiated with 2.5μm, 5.0μm, 7.5μm, 10.0μm spot sizes. Again, the spot size dependence is of interest here, together with a comparison to the results in the thicker film case (Case 2 above).

Figures [4.3.6] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 300 nm-thin aluminum film on BSG under low-vacuum conditions using spot sizes of 2.5μm. Figure [4.3.6] (a) is at a fluence of 0.6J/cm² results in the formation of small round bumps, Figure [4.3.6] (b) at 1.0J/cm² holes are formed around the ring.
Figure 4.3.6: SEM images of a 300 nm-thick aluminum film with a BSG substrate irradiated with a 2.5 μm spot at different fluence levels.

Figures [4.3.7] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 300 nm-thick aluminum film on BSG under low-vacuum conditions using spot sizes of 5.0 μm. Figure [4.3.7] (a) at a fluence level of 0.4 J/cm² results in the formation of small holes around the bump, Figure [4.3.7] (b) at 0.9 J/cm² ablation holes are formed.
Figure 4.3.7: SEM images of a 300 nm-thick aluminum film with a BSG substrate irradiated with a 5.0 μm spot at different fluence levels.

Figures [4.3.8] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 300 nm-thick aluminum film on BSG under low-vacuum conditions using spot sizes of 7.5μm. Figure [4.3.8] (a) at a fluence levels 0.5J/cm² results in the formation ablation holes with rough edges some kind of random protrusion at the ends of the hole, Figure [4.3.8] (b) at 0.9J/cm² holes are formed.
Figure 4.3.8: SEM images of a 300 nm-thick aluminum film with a BSG substrate irradiated with a 7.5 μm spot at different fluence levels.

Figures [4.3.9] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 300 nm-thick aluminum film on BSG under low-vacuum conditions using spot sizes of 10.0μm. Figure [4.3.9] (a) at a fluence level of 0.4J/cm² results in the formation of holes with randomly located sized protrusions at the edge of the holes, Figure [4.3.9] (b) at 0.9J/cm² ablation holes are formed.
Discussion: In all of the above cases although protrusions were not observed in these films, irradiation at low fluence levels does result in the formation of the microbumps with small central holes. These central holes are due to the removal of material most likely through evaporation, or surface deformation. The formation and the ejection of droplets appear to be unlikely, since no individual loose or attached droplets were ever observed in the vicinity of the irradiation spots.
4.4 Irradiation of Titanium Films

Titanium has the lowest thermal conductivity and the highest melting point among all metals examined in this project. Titanium films do not appear to form regular-shape structures of any kind at any irradiation conditions. A detailed study on localized single-pulse irradiation of Ti films was performed and some of the results are presented and discussed below.

CASE 1:

In this case we present images of microstructures obtained as a result of single-pulse laser irradiation of a 730nm thick titanium film with a BSG substrate irradiated with 7.5μm spot size at different fluence levels.

Figures [4.4.1] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 730 nm-thick titanium film on BSG under low-vacuum conditions using spot sizes of 7.5μm.
Figure 4.4.1: SEM images of a 730 nm-thick titanium film with a BSG substrate irradiated with a 7.5 μm spot at fluence levels (a) 0.34J/cm² and (b) 0.71J/cm².

**Discussion:** As seen from Figure [4.4.1] titanium films do not appear to form microbumps at any fluence level. Instead, a thin portion of the films surface appears to have become molten and roughened, and some of the material is vaporized/ablated. Because of the lower thermal conductivity of titanium, it is thought that the heat is confined to the surface of the film causing superheating and ablation.

**CASE 2:**

In this case we present images of microstructures obtained as a result of single-pulse laser irradiation of a thinner 250nm thick titanium film with a BSG substrate irradiated with 2.5μm, 5.0μm, 7.5μm, 10.0μm spot sizes.
Figures [4.4.2] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 250 nm-thick titanium film on BSG under low-vacuum conditions using spot sizes of 2.5μm. Figure [4.4.2] (a) at a fluence level of 0.4J/cm² the surface becomes molten and roughened as result of the removal of material through evaporation/ablation. In Figure [4.4.2] (b) at 0.9J/cm², there is hole formed in the center of that molten area, as a result of even more significant removal of material.

![SEM images of microstructures](image1)

(a) 250nm Ti on BSG, 0.4J/cm²  
(b) 250nm Ti on BSG, 0.9J/cm²

Figure 4.4.2: SEM images of a 250 nm-thick titanium film with a BSG substrate irradiated with a 2.5 μm spot at different fluence levels.

Figures [4.4.3] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 250 nm-thick titanium film on BSG under low-vacuum
conditions using spot sizes of 5.0μm. Figure [4.4.3] (a) at fluence levels 0.3 J/cm² the surface becomes molten and randomly shaped openings formed, Figure [4.4.3] (b) at 0.9 J/cm² represents a similar outcome but with even larger craters and holes are forming. A level of film delamination is observed in both cases.

Figure 4.4.3: SEM images of a 250 nm-thick titanium film with a BSG substrate irradiated with a 5.0 μm spot at different fluence levels.

Figure 4.4.3: SEM images of a 250 nm-thick titanium film with a BSG substrate irradiated with a 5.0 μm spot at different fluence levels.

(b) 250nm Ti on BSG, 0.9J/cm²

Figure 4.4.3: SEM images of a 250 nm-thick titanium film with a BSG substrate irradiated with a 5.0 μm spot at different fluence levels.

Figures [4.4.4] includes SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 250 nm-thick titanium film on BSG under low-vacuum conditions using spot sizes of 7.5μm. Figure [4.4.4] (a) at fluence levels 0.2 J/cm² surface
is roughened and molten, randomly shaped openings form, together with film
delamination, and in Figure [4.4.4] (b) at 0.9 J/cm$^2$ a similar outcome is observed, but
with larger opening revealing the surface of the substrate.

![SEM images of a 250 nm-thick titanium film with a BSG substrate irradiated with a 7.5 μm spot at different fluence levels.](image)

(a) 250nm Ti on BSG, 0.2J/cm$^2$  
(b) 250nm Ti on BSG, 0.9J/cm$^2$

Figure 4.4.4: SEM images of a 250 nm-thick titanium film with a BSG substrate irradiated with a 7.5 μm spot at different fluence levels.

Figures [4.4.5] includes SEM images of microstructures obtained as a result of
single-pulse laser irradiation of a 250 nm-thick titanium film on BSG under low-vacuum
conditions using spot sizes of 10.0μm. As seen from the Figure holes are formed on the
surface of the titanium film at different fluence levels at 10.0μm spot size.

![SEM images of microstructures obtained as a result of single-pulse laser irradiation of a 250 nm-thick titanium film on BSG under low-vacuum conditions using spot sizes of 10.0μm.](image)

(a) 250nm Ti on BSG, 0.3J/cm$^2$  
(b) 250nm Ti on BSG, 0.9J/cm$^2$

Figure 4.4.4: SEM images of a 250 nm-thick titanium film with a BSG substrate irradiated with a 10.0 μm spot at different fluence levels

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Discussion: In case (2) titanium films when irradiated using lower spot size of 2.5μm do not appear to form microbumps at any fluence level. Instead, a thin portion of the films surface appears to have become molten and vaporized. But when the substrate is irradiated using 5.0μm spot size or larger, in addition to the surface melting and roughening a significant level of film delaminaiton is observed.

4.5 Temperature Profile Evolution Simulation

To better understand the flow of laser generated heat through the various film and substrate combinations examined in this work, COMSOL Multiphysics was used to provide numerical solutions to the heat transfer equations. COMSOL Multiphysics (formerly FEMLAB) is a finite element analysis and solver software package for various physics and engineering applications, especially coupled phenomena, or multiphysics. COMSOL Multiphysics also offers an extensive and well-managed interface to MATLAB and its toolboxes for a large variety of programming, preprocessing and post processing possibilities. A similar interface is offered to COMSOL Script. In addition to conventional physics-based user-interfaces, COMSOL Multiphysics also allows for entering coupled systems of partial differential equations (PDEs). The PDEs can be entered directly or using the so called weak form.

There are several application modes like in COMSOL multiphysics

- AC/DC Module.
- Chemical Engineering Module.
- Heat Transfer Module.
- MEMS Module.
• RF Module.

• Structural Mechanics Module.

We used the Heat Transfer Module. The *Heat Transfer Module* is an optional package that extends the COMSOL Multiphysics modeling environment with customized user interfaces and functionality optimized for the analysis of heat transfer. In the Figure shown below, point A is considered on the substrate where the fluence level at the central part of the irradiation spot (contact boundary), while the central melted part continues stretching in the direction normal to the substrate with the formation of the nanojet, point B is considered on the left part of the structure formed, point C is considered at central part of the structure formed, and point D is considered on the right part of the structure formed.

The model below is a 500nm thick Ti film on borosilicate glass irradiated with a spot diameter of 2.5 μm. The blue region indicates the irradiated surface with a spot diameter of 2.5 μm using a laser pulse (representated in the model by a heat source pulse) with a *top-hat spatial profile* and a *Gaussian temporal profile*; and the yellow region indicates the non irradiated surface where each yellow region extends 10um beyond the spot periphery. The initial temperature is 300K temperature profiles as a function of time start at an initial temperature of 300 K, and the laser pulse maximum arrives 9ns after the beginning of the simulation at t=0. The pulse duration (FWHM) is 7ns. The bottom and side walls of the simulated volume are kept at room temperature (i.e., isothermal T = 300K boundary conditions).
Figure 4.5.1: Schematic representation of the computational setup used in MD–TTM calculations.

**COMSOL Model:**

Even though the simplified modeling presented above does not account for phase changes or film expansion or movement, these results are still useful in understanding the formation of the various microstructures on different metal films, described above. In this model, appropriate thermal properties and boundary conditions were defined for each of the different segments as explained above.

Figure [4.5.2] shows the results of the finite element modeling of titanium film single-pulse irradiation (i.e., deposition of heat and the evolution of the resulting temperature profiles). This figure shows the effect of irradiation at different points such as A, B, C and D represented by the different colors.
Cu

High: Red=A, Green=C, Blue=D

Inter: Red=A, Green=C, Blue=D
Low: Red=A, Green=C, Blue= D

Figure 4.5.2: Simulation results from the finite element modeling showing irradiation at different points (i.e., A, C, and D) on a copper film at different fluence levels (i.e., High, Intermediate, and Low).

High: Red=A, Green=C, Blue= D (D is equivalent to B)
Figure 4.5.3: Simulation results from the finite element modeling showing irradiation at different points (i.e., A, C, and D) on a titanium film at different fluence levels (i.e., High, Intermediate, and Low).
Comparison:

**Cu**: Blue = A, Red = C and D

**Ti**: Blue = A, Red = C and D

Figure 4.5.4: Comparison of simulation results from the finite element modeling showing irradiation at different points on titanium and copper films at intermediate fluence level.
**Discussion:** The results of the finite element modeling for the titanium tips can be seen in the Figures [4.5.2] above. As seen, from the graphs at different fluence levels the temperature increases to maximum with increase in the fluence level. And at point C the temperature is maximum. From the figure at high fluence it is clear that the temperature at point A just exceeds the melting point of Ti and at points C and D it is way above the melting point of Ti. Hence, this might be one of the reasons for the surface melting and eventually the formation of microstructures and sharp protrusions, when a single pulse laser irradiation is done on the surface of the substrate.

Also the finite element modeling for copper melting in Figure [4.5.3] is done in a similar fashion. From the graphs it is seen that the temperature at point A exceeds the melting point and at points C and D it is also above the melting point of Cu and remains there for a relatively long time, which is very different from the Ti film case.

In Figure [4.5.4] a comparison has been made between copper and titanium irradiated at intermediate fluence level. Several observations can be made. First, as mentioned above the bottom part of the Ti film does not reach the melting point, so Ti is only partially melted close to the surface, whereas the copper film (due to its much higher thermal conductivity, almost always is melted through its entire thickness (certainly so in the central part of the spot). Second, the lateral temperature gradient seems to be indignant in the Cu film case as evidenced by the negligible T-difference between the center top temperature and the peripheral-top temperature (blue and green lines), whereas in case of the Ti film, there is a noticeable difference, and a more significant gradient. Again this can be attributed to the thermal conductivity difference, although the explanation is not so straightforward given the role of the surrounding material in taking
heat away from the irradiated volume. Third, the bottom and the top surfaces see their temperature maxima very closely in time in the Cu film case, whereas there is substantial delay in the Ti-film case.

Overall, these simplified modeling results suggest that melting through the entire film thickness is substantial in the formation of the structures that are obtained upon irradiation of Cu films on borosilicate glass substrates. These results are of even more direct use in understanding the modifications of the Ti films upon irradiation – the low thermal conductivity provides for local surface melting and overheating of the Ti film and therefore evaporation/ablation openings are observed. When the laser fluence is very high, the rapid heat deposition combined with the brittle nature of the Ti film could also lead to the experimentally observed film delimitation and cracking around and within the ablation spot.
Chapter 5

Conclusions

Our results show that within certain range of fluence values, irradiation spot sizes and film thicknesses, it is possible to fabricate various round, almost spherical microbumps sharp high-ratio protrusions with single pulse laser irradiation in case of gold or copper films. The shapes and sizes of both types of structures have been shown to be controllable via adjustment of various laser, film and geometry parameters. However, the controllability in the case of Cu is not as good as that in the case of Au.

In the case of Al films, we were not able to find conditions for the formation of sharp protrusions. On the other hand, round-top microbumps could be formed in a very controllable way within a wide parameter range of laser spot sizes, and laser fluences. Our results therefore have given evidence that this single-pulse localized laser irradiation bases method can be used as the basis of a sample, cost-effective technology for the fabrication of large dense arrays of such structures on Au, Cu or Al films.

In the case of Ti films, we have not found evidence for the formation of bumps, or sharp structures of any kind. Instead, in all cases when the laser fluence exceeds a threshold value, a roughened-surface ablation spot forms and develops into an ablation opening at higher fluencies.
The results from temperature profile evaluation simulations are useful in understanding the formation of the various microstructures on different metal films. The evolution of the temperature profiles obtained as result of solving numerically the heat transfer equation, indicate a predominately lateral heat flow in the case of both copper films and titanium films. The profiles obtained are in a qualitative agreement with the fact that film melting is a required first step in the formation of the structures observed in the Cu film case. From this modeling it is also clear that the low thermal conductivity of Ti is instrumental in obtaining the type of surface modification that we see experimentally.

This research has proved that the single-pulse localized laser irradiation based technique is capable of fabrication micro-and nano-structures on thin metal films. Future studies are needed in a variety of areas to explore fully the types of structures that are possible on other film-substrate combinations and to get a better understanding of the formation processes.
References


37. Paul Scherrer Institut,  


44. K. Anselme, M. Bigerelle, B. Noel, E. Dufresne, D. Judas, A. Lost, P. Hardouin.
   “Qualitative and quantitative study of human osteoblast adhesion on materials with

   on silicon nanostructures." *Journal of Vacuum Science and Technology B*, vol. 15, no. 6,

   and W Shain. "Attachment of astroglial cells to microfabricated pillar.”

   "Investigation of cell reactions to microstructured implant surfaces." *Materials Science

   Pattern in Culture." *Developmental Brain Research*, vol. 51, pp. 128-131,

49. S Thanawala, O Palyvoda, D G Georgiev, S P Khan, I A Al-Homoudi, G Newaz, and G

   Berling Heidelberg: Springer-Verlag, 2006.


52. S Nie and S R Emory. "Probing Single Molecules and Single Nanoparticles by


60. J.P. Moening, D.G. Georgiev, J.G. Lawrence, to appear in *Journal of Applied Physics*