MICRO/NANO PATTERNING OF SILICON AND NiP/Al DISKS BY NANOSECOND AND FEMTOSECOND LASER SOURCES

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ANA AZUCENA PEÑA ALVAREZ

School of Mechanical, Aerospace and Civil Engineering
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**NOMENCLATURE**

A  area (m$^2$)

$A(\lambda)$  spectral absorption

a  particle radius (µm)

c$_0$  speed of light (299,792,458 m s$^{-1}$)

D  beam diameter (m)

$D_L$  beam diameter before the lens (m)

d$_{\text{min}}$  spot diameter containing 86% of focused energy (m)

E  energy (J)

$E_Y$  Young’s modulus of elasticity (Pa)

$\tilde{E}$  electric field (N C$^{-1}$)

F  f-number, focal ratio

$F_{\text{th}}$  laser fluence threshold (J cm$^{-2}$)

f  focal length (m)

h  Planck’s constant ($6.62606957 \times 10^{-34}$ J s)

I  light intensity (W cm$^{-2}$)

$J_{\text{sc}}$  short-circuit current density (mA cm$^{-2}$)

K  Boltzmann constant (1.3806488 x $10^{-23}$ J K$^{-1}$)

$N_1$  number of atoms in the ground state

$N_2$  number of atoms in the excited state

n  refractive index

P  pressure (N m$^{-2}$)

q  electron charge ($1.60217646 \times 10^{-19}$ C)

R  Rayleigh range (m)

$R_a$  average surface roughness (µm)

R($\lambda$)  spectral reflectance

Re[$S_z$]  normalised Poynting vector

S($\lambda$)  solar energy distribution

s  scanning speed (m s$^{-1}$)

T  temperature (K)
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**Greek characters**

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<td>$\omega$</td>
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This PhD thesis presents the outcome of employing both nanosecond and femtosecond pulsed lasers in order to modify the surface structure of a material at the micro and nano scales. Literature review was carried out on micro/nano fabrication technologies involved in the semiconductor industry, which are the basis of many current micro and nano-manufacturing processes.

The first experiments concentrated on direct laser scanning of Si to produce surface microstructures. This type of texturing was very effective at reducing surface reflectivity and can be implemented in photovoltaic devices. It was also found that the ablation efficiency can be improved if laser processing is performed in an argon environment where oxidation can be suppressed. Moreover, a significant relationship between laser-texture characteristics (i.e. topography/morphology and periodicity) and total surface reflectance was demonstrated. Short-circuit modelling of the laser-texture showed that electrical performance of the cell can be improved by 41.3% in the 360-1100 spectrum, even in the near-infrared for which Si is a weak absorber.

From these experimental results, it was also noticed that the laser-generated micro-structures made the surface significantly wettable; but as the laser fluence was reduced, the contact angle of the surface could be changed. This led to the investigation of the wetting properties of nano-bumps produced on Si at fluences below the ablation threshold. Their wetting behaviour was reported for the first time. An effect named as ‘invisible marking’ in this thesis was demonstrated: vapour condenses into water drops of different size depending on the lattice arrangement of c-Si or a-Si. Such an interaction at the near-ablation threshold was also explored for another type of material: NiP/Al data storage disks. From this research, elliptical bumps with vertical dimension in the sub-nanometre scale were fabricated with extremely high repeatability (± 0.4 nm). In addition, it was found that elliptical bumps can offer better stiction performance than circular shapes, even at ultra-low flying height. This type of laser texture could be utilised as a means for tribological optimization of surfaces that are in close proximity and relative motion.

Following the use of low-fluences by nanosecond pulses, this was also applied to scanning over a microsphere lens array. So far, the research on near-field effects produced at the bottom of transparent particles has focused on how to generate parallel nano-patterns by single pulses. However, the present work has demonstrated that a focused beam with a tight-focus can be used to fabricate single lines or shapes rather than repeated patterns. In this way, a femtosecond laser was introduced to meet such a challenge. Moreover, laser-induced periodic surface structures (LIPSS) by fs pulses were also identified along the near-field generated nano-patterns. The evolution of such a periodic, self-assembly structuring was also investigated, and new optical characteristics of structural colour were found.
DECLARATION

I hereby declare that no portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

2011

Ana Azucena Pena Alvarez
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ACKNOWLEDGEMENTS

First I want to dedicate this thesis to my Lord and my God Jesus Christ who said: “I am the Alpha and the Omega, the Beginning and the End,” says the Lord, “who is and was and who is to come, the Almighty” (Revelation 1:8). Without Him in my life I would not have been able to pursue this doctoral degree. I have committed my future to the Lord and I will wait on Him.

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LIST OF PUBLICATIONS

Journal Papers


Conference Papers


Conferences and Awards


2010  1st Place Young Academic Entrepreneur Award 2010, Nuevo Leon, Mexico.

2010  Oral Presentation at the “Photonics and Materials North West Conference”, April 14th, Liverpool, UK.

2009  1st Place Poster Presentation Award by the Laser Institute of America at the 28th International Congress on Applications of Lasers & Electro-Optics ICALEO 2009, November 2nd – November 5th, Orlando, FL.

CHAPTER 1

INTRODUCTION

1.1 Research Motivation and Rationale

Manufacturing at the nanoscale includes all materials, processes and equipment employed for the fabrication of nanoscale structures, features, devices and systems in one, two and three dimensions. It comprises two approaches: bottom-up and top down. In the first one, assembly of nanostructure building blocks (individual atoms and molecules) takes place, while in the second one, material is manipulated with specialized instruments [1]. The manipulation of materials to modify their molecular architecture and morphology can, for example, enable the control of their electronic and optical properties and also facilitates their processability [2].

Nanomanufacturing applications are found in the field of integrated optoelectronic coupling, integrated circuit fabrication, surface treatment, data storage and lithography techniques, amongst many others. The development of such fields demands an urgent improvement in resolution and precision of photosensitive technologies. Current conventional photoprocessing techniques are constrained in lateral resolution by the spot size of the light source. The smallest size of the structures fabricated by these techniques is situated on the submicron scale because of the diffraction limit of light. An effective way to overcome this limit is to employ the effects of an optical near field, which offers better precision, finer resolutions and an enhanced capability for photoprocessing in the nanometre regime [2].

Due to the advent of new and improved nanofabrication techniques, patterns in the sub-diffraction limit range are possible. The adequate use of those techniques resides in the intended nanopatterning application, which might fall in one of the following areas: nanoelectronics [3-5], nanophotonics [2, 6], plasmonics [7-9],
nanomaterials [7], photovoltaics [8, 9], tissue engineering [10, 11], orthopaedics [12-15] and biomedics [16, 17].

It is of primary importance that the manufacturing of nanostructures can be achieved at a low cost, high throughput, with simple setups and good resolution. Depending on the desired results, several methods can be implemented: from Electron Beam Lithography (EBL) and Focused Ion Beam (FIB) Lithography to near-field patterning. All these methods present advantages as well as limitations depending on the purpose of fabrication.

1.2 Aim and Objectives of the Research

The aim of this project was to understand nano-second and femto-second pulsed laser interactions with engineering materials especially at fluences below the ablation threshold and to identify material characteristics after laser processing. It was intended to establish the feasibility of using a diode-pumped Nd:YVO$_4$ laser and a Ti:Sapphire laser as efficient tools for micro and nano-patterning of materials like silicon and NiP/Al disks in micro/nano scales.

Considering this, prioritised project objectives are listed as follows:

- Laser micro-texturing of silicon, to reduce reflectivity and to prompt an absorption enhancement in solar cells.
- Laser nano-texturing of silicon to modify its wetting characteristics for security tagging and its potential application in micro/nano fluidic devices.
- Laser texturing of NiP/Al hard disks for improved stiction performance.
- Laser direct writing of micro/nano scale patterns to achieve single lines/user-defined patterns.
- Femto-second laser structuring of silicon for structural colour/photonics applications.
The outcome of this work pursues the potential for further translation of micro and nano-research progress into industry.

1.3 Thesis Outline

In the present research work, various suitable laser micro/nano fabrication technologies that have the potential to be developed and scaled to an industrial environment were investigated by means of nanosecond and femtosecond laser sources. To achieve nano-structuring it was necessary to understand how laser light interacts with the material at larger scales. For this reason, experiments began with fluences above the melting/ablation threshold for nanosecond pulses. By lowering the energy density delivered to the substrate (i.e. Si, NiP/Al), material modification at the nanoscale was possible in the vertical dimension, down to 1 nm and sub-nm features. One of the most relevant outcomes from this research was the recognition of a practical function for these ultra-low height structures.

Once the near-ablation threshold for the material was identified, pulsed laser irradiation was combined with near-field effects of a microsphere array to ablate the material at the nanoscale in 3D. Conventionally, near-field techniques provide patterning of large areas with parallel nano-structuring, but the need to achieve single patterns motivated this research to employ a tight focused beam to scan lines or arbitrary, user-defined shapes composed of nano-craters/bumps. Femtosecond pulses offered superior quality finish, and also produced a double-scale texturing on the surface of the material, by the generation of laser-induced periodic surface structures (LIPSS). These were also fabricated without the use of a contact particle array, and nano-engineered in such a way that a structural colour effect was produced. This optical effect is the same as the one displayed by the colourful, iridescent wings of a butterfly.

Chapter 2 focuses on the main processes in the microelectronics industry. It was necessary to include this information because many non-laser and laser nano-
manufacturing methods share several of those processing steps (e.g. film deposition, optical lithography, and etching). Moreover, the photovoltaic industry is based on many of these substrate preparation methods. This chapter also reviews recent research in non-laser nano-fabrication techniques. Some of the methods include the use of Electron Beam Lithography (EBL), anodization processes, colloidal crystals as a mask, conformable phase masks, embossing and Atomic Force Microscopy (AFM).

Chapter 3 gives a brief overview of laser physics fundamentals, laser beam characteristics and focusing optics. Current laser nano-fabrication techniques are also presented. Nanometre scale nano-manufacturing can be achieved by means of laser sources and methods such as interferometric lithography and femtosecond laser irradiation. Also, various near-field effects techniques are discussed: optical chemical vapour deposition, Scanning Probe Microscopy, Near-Field Scanning Optical Microscopy and Contact Particle Lens Array (CPLA) patterning.

Chapter 4 describes the experimental and analytical apparatus utilised during the course of this research work: laser sources, surface characterisation equipment and spectrophotometric devices.

Chapter 5 reports experimental work on silicon micro-texturing using a diode pumped Nd:YVO₄ laser system with a computer controlled 2 axis galvanometer beam scanner. High laser scanning speeds (~1 m/s) were applied and KOH etching was implemented after laser processing to clean the surface of any unwanted debris that might deteriorate the optical and electrical characteristics of the material. The effect of several scanning passes on the depth of the structures is also explored and quantified. Experiments were also performed under an argon environment which was demonstrated to increase the ablation efficiency of the process. In addition, contact angles were measured to further investigate the wetting properties of the textured surfaces. Structures resulted in completely hydrophilic surfaces. However, it was noticed that structures at low fluences and after a single scan presented a change in wettability different from the one characteristic of bare,
untreated Si. This led to notice an ‘invisible marking’ effect, which was studied in depth and is presented in Chapter 6.

**Chapter 6** details the work done on debris-free laser marking by generation of c-Si nano-bumps. By rapidly scanning a Nd:YVO₄ laser, frequency doubled to emit at 532 nm in the nano-second pulse regime and below the ablation threshold, a uniform array of nano-bumps of less than 2 nm height (diameter around 20 µm) have been generated on crystalline Si. They were generated at 30,000 bumps per second. The effect of laser fluence (energy density) and scanning speed on the characteristics of the nano-bumps was investigated and the wettability of the laser nano-textured surfaces was analysed. The mechanisms of nano-bump formation are discussed. The application of the technique for debris free invisible marking/texturing of silicon and recognition of the marks/patterns are presented.

**Chapter 7** introduces nano-scale height elliptical bumps on a nickel-phosphorous coated aluminium (NiP/Al) disk. Such bumps were fabricated by a diode pumped Nd:YAG laser beam. By varying laser fluences, scanning speeds and repetition rate, the nano-bump height can be controlled below 10 nm down to the sub-nm level. Mathematical modelling was carried out to demonstrate how this type of laser-induced texture on a disk surface can provide improved stiction control when the head slider flies over the disk at an ultra-low height.

**Chapter 8** presents a modification to a micro-nano patterning technique. It is based on the laser patterning by scanning a focused laser beam through a self-assembled monolayer of silica microspheres on a single-crystalline Si substrate. Following the surface and monolayer preparation, a diode pumped Nd:YVO₄ laser system with a computer controlled 3 axis galvanometer beam scanner was employed to write user-defined patterns through the particle lens array on the Si substrate. After laser irradiation, the obtained patterns, which are in the micro-scale, were entirely formed by nano-structures, either holes or bumps depending on the laser fluence and scanning speed utilized. This is reported for the first time. The pattern resolution depends on the size of the microsphere and the scanning laser beam. Similar experiments were carried out by means of a femtosecond laser source which revealed
better surface finish structures, along with the presence of periodic ripples generated at certain fluences. This type of surface modification is studied in more detail in chapter 9.

Chapter 9 gives an account of the evolution of laser-induced periodic surface structures (LIPSS) on silicon by single and multiple femtosecond pulses. It is suggested that an incubation effect is responsible for ripple generation by multiple pulses at fluences below the ablation threshold by a single pulse. The mechanism behind the origin of ripples is discussed and an ‘invisible marking’ effect detected in laser-induced amorphous areas is also presented.

Chapter 10 introduces the optical effects of the LIPSS detailed in chapter 9. Several structural colour properties are accomplished by nano-engineered femtosecond structuring: iridescence, intensity modulation, stretching/compressing and a forward/delay colour shift in the visible spectrum.

Chapter 11 provides conclusions for the research work of this thesis. A discussion on the continuation of the outcome of this thesis is proposed by a list of suggestions for future work.
CHAPTER 2

REVIEW OF MICROFABRICATION PROCESSES IN THE SEMICONDUCTOR INDUSTRY AND NON-LASER MICRO/NANO FABRICATION TECHNIQUES

2.1 Introduction to Processing of Semiconductor Materials

In order to better describe micro and nanofabrication techniques it is essential to define some of the basic processes that take place in microfabrication, used mainly in the microelectronics industry [18].

The size of the features involved in microfabrication range from several micrometers to some tens of nanometres. So, important consideration must be paid to the elimination of particles like dust, smoke and bacteria that can affect the correct functioning of an integrated circuit. Clean rooms are essential in the microelectronics environment. Class 1 to class 10 is the range of clean rooms used in this industry, class-10 clean room having 10 or fewer particles (size of 0.5 micrometers or larger) per cubic foot [19].

One of the widest used materials in the semiconductor and photovoltaics industries is silicon [20]. In order to obtain single-crystal and defect free material a crystal growing and wafer preparation process is necessary. First, silica and carbon are heated producing 95 to 98% pure polycrystalline silicon. Then a step known as Czochralski process is applied in order to get single-crystal silicon which starts by
dipping a seed crystal into molten silicon. Then the seed is pulled out from the melt at the same moment it is spun around its axis. The final product is a cylindrical single-crystal ingot. This ingot undergoes a series of machining and finishing processes in order to obtain silicon wafers. These processes are described as follows [19]:

### 2.1.1 Film Deposition

Film deposition is the first operation performed on the silicon wafer. Films can be insulating or conducting, and among most used materials are poly-silicon, silicon nitride, silicon dioxide, titanium and aluminium. The deposited film has the functionality of masking and protecting the substrate. Film deposition can be prepared by evaporation, sputtering, chemical vapour deposition (CVD) or electro-deposition [19, 21].

### 2.1.2 Oxidation

Oxidation occurs due to the reaction of oxygen with the substrate material. Oxide films that are grown by thermal processes exhibit higher levels of purity than the ones elaborated by deposition techniques. The reason for this is that they are directly grown from a high quality substrate. Dry oxidation develops when the substrate temperature is raised from 750°C to 1100°C inside an oxygen environment. Wet oxidation results from a water-vapour atmosphere. Its main defect is a low oxide density and consequently, a lower dielectric strength. Selective oxidation occurs when only some parts of the substrate are to be oxidized; it makes use of silicon nitride to cover selected parts which restricts oxygen and water vapour from reaching the substrate surface [19].
2.1.3 Optical Lithography

One of the well established and most suitable process for semiconductor and MEMS fabrication is conventional optical lithography, but its major disadvantage lies on the diffraction limit of light, so its use in nanofabrication is hampered [22]. Lithography is the process of transferring patterns to a substrate surface. Photolithography uses masks to transfer patterns to the wafer through a lens system [23]. Masks can be made of glass or quartz plates, with the pattern deposited on to them by means of a chromium film [19].

Photoresists are organic polymers coated onto the wafer after the film deposition process. They change their structure when exposed to radiation with the help of a sensitizer that controls the reactions in the polymer. Also a solvent is used to spread the polymer in liquid form. Photoresists are extended over the substrate by spin coating at several thousand rpm for 30 to 60 seconds. By prebaking the wafer, solvent is removed and photoresist is hardened [19].

Pattern transfer is done by stepper or step-and-scan systems. During wafer stepper, the complete image is exposed in one flash, and then is refocused to a contiguous section. In step-and-scan, the light source is fixed to a point while the mask and wafer are moved in opposite directions [23]. In both methods, UV radiation is focused at the reticle and after development and removal of the exposed sections of the photoresist, the transferred pattern is obtained. Reticles can figure a negative or a positive pattern. Positive reticles permit UV radiation to break down the chains in the polymer film followed by its subsequent development. As a final step, stripping is employed to dissolve the developed photoresist by using acetone or strong acids. Also oxygen plasma can be utilized. Etching will remove the underlying film not covered by the photoresist [19].
2.1.4 Extreme ultraviolet lithography

Deep-ultraviolet projection lithography can pattern two dimensional structures on a large scale and is able to create any pattern in just a single exposure step. Some of its disadvantages are that it is a costly process and involves complex optics to obtain an aberration-free imaging of the mask (Figure 2.1). Due to the small depth of focus, deep-ultraviolet projection lithography requires a complex focusing system and its mask has to be written by e-beam lithography [24].

![Figure 2.1 Simple EUV imaging system showing the mask, imaging optics, and wafer [25]](image)

Extreme ultraviolet lithography uses a light wavelength of 13 nm to reduce the effect of diffraction and enhance smaller resolution sizes than those achieved by photolithography. By using a two mirror Schwarzschild imaging system, the pattern from the mask is imaged with a 10:1 reduction ratio onto a resist-coated wafer surface [19, 25].
2.1.5 X-ray beam lithography

X-ray beam lithography uses shorter radiation wavelengths and a larger depth of focus than photolithography which can produce very fine patterns in thick resist. It is not so susceptible to dust, and the aspect ratio can be extended to 100, compared to the aspect ratio of 10 offered by conventional lithographic techniques. It can deliver high throughput when combined with the LIGA process (x-ray lithographie, galvanof ormung und abformung (german): x-ray lithography, electrodeposition, and moulding). However, x-ray beam lithography requires synchrotron radiation which is expensive and not readily available [19]. Other concerns regarding this technology are its specialised mask membrane fabrication process, and the advanced alignment system it requires to control the narrow membrane-resist gap [26].

2.1.6 Electron beam lithography

Electron beam lithography allows nanofabrication with resolution as small as a few nanometres. But some drawbacks of this technique are that it needs expensive samples, vacuum conditions, and because of it serial nature, low processing speed [27]. It employs high current density in a narrow electron beam which can be scanned over the wafer to pattern one pixel at a time. Masking is achieved by controlling the point-by-point transfer utilizing a specialized software [19].

2.1.7 Focused Ion Beam lithography

Focused Ion Beam (FIB) is a maskless lithography technique that employs a ion beam of Ga to nanopattern with numerous applications including photonic devices like distributed Bragg reflectors (DBR), 1D and 2D crystals and surface plasmon waveguides. Inconveniences of the process are material re-deposition and incident ion beam contamination. Another negative aspect is that due to the beam shape, the milled structures exhibit a conical profile [19].
The resolution of the patterns obtained with FIB is given by the spot size which can be as small as 7 nm resulting in typical lateral sizes of 10 nm. The beam spot size varies with the ion beam current which has a range of 1 pA to 40 nA. Nanohole arrays can be created on an epitaxial layer of SiO$_2$ on an n-GaAs substrate. This mask is used to attain vertical sidewalls combined with dry etching to avoid the typical conical profile and to eliminate re-deposition. To avoid surface charging an ultra thin film of titanium is deposited on top of the sample which is removed during dry etching. Later, the dielectric mask is selectively removed [19].

In FIB milling, dwell time affects the diameter and depth of nanopatterns. Having a fixed total milling time, if the dwell time is reduced, the number of scans per perforation increases which results in an enlargement of the overall size. To achieve smaller nanostructures it is recommended to use a longer dwell time (with reduced total milling time) and a small current [19].

### 2.1.8 Etching

Etching can be defined as the process in which particular areas of films are removed. Selectivity during this step is a crucial factor and is denoted by the ability to etch one material without deteriorating another. Wet etching consists of immersing the wafer into an acidic liquid solution, and as it is an isotropic process, removal of material occurs in all directions at the same rate. During this type of etching undercuts below the mask are obtained, degrading the resolution of patterns in the substrate. Anisotropic etching (i.e. unequal removal of material along different directions) occurs when etching depends on composition or structural variations in the material [19].

Dry etching is done by utilizing chemical reactants in a low-pressure system. It achieves high directionality, offering well defined profiles. Sputtering etching is a dry etching technique where the film is bombarded with noble gas ions. The ionization occurs by means of a cathode and an anode, and material is etched away because of a bond-breakage mechanism when the ions impinge on the surface [19].
Reactive plasma etching or dry chemical etching use RF excitation to generate chlorine or fluorine ions that diffuse and react with the substrate, forming a volatile compound removed from the plasma reactor by a vacuum system. Physical-chemical etching includes reactive ion-beam etching (RIBE) and chemically assisted ion-beam etching (CAIBE). They use chemically reactive species to etch away material, assisted by ion sputtering. RIBE is also called deep reactive-ion etching (DRIE). Also because the ion targeting is directional, etching becomes anisotropic and does not affect mask material [19].

2.1.9 Diffusion and Ion Implantation

As a final step involved in microdevice fabrication, diffusion and ion implantation have to be described due to their importance in the semiconductor industry. Electrical properties of some regions in the substrate can be induced thanks to the introduction of dopants by means of diffusion and ion-implantation processes. During diffusion, dopants are introduced to the substrate by depositing a film or by immersing the substrate in a vapour containing the dopant. Drive-in diffusion is used to attain a more even concentration of dopants within the substrate by heating the wafer. The main drawback of diffusion is its highly isotropic results. Ion implantation is a process in which ions are accelerated through a high voltage field and the desired dopant is selected with the aid of a mass separator. Annealing after ion implantation provides repair of the silicon surface damaged during the process, it also enhances further diffusion of the dopants into the substrate [19].

2.2 Micro/Nano Structuring of Materials and Applications

Recent techniques that are employed to modify materials at the micro/nanoscale are presented. A selection of state of the art work in the field of micro/nano patterning by colloidal self-assembly, direct contact printing and near-
Chapter 2-Review of Microfabrication Processes

field effects was selected due to its relevance to the experimental work undertaken during the course of this thesis.

2.2.1 Natural/Colloidal Lithography

Natural or colloidal lithography refers to a self-organizing process [28]. The first work in this area was done by Fischer and Zingsheim in 1981. They proposed “naturally” assembled polystyrene latex nanospheres as a mask for contact imaging with visible light [29]. Disadvantages of this technique are its homogeneous nature, restriction to elaborate complex nanostructures and the appearance of defects because of thermodynamic phenomena [30].

Another type of colloidal lithography consists of a dispersed monolayer of nanoscale spherical particles (e.g. latex or SiO$_2$ micro-spheres) that is self-assembled on top of a substrate and heated above the glass transition in order to modify the shape of the individual particles. Then, using a collimated argon ion beam, the surface is dry etched and the pattern of the individual particles is transferred into the surface. As a result, ordered arrays of gold cylinders are left on a substrate. The particles remaining on some of the cylinders are removed by exposure to ozone. This technique can be used to template a nano-pattern of proteins which are then immobilized and used as detection systems, stimulatory cues for biosystems or as model systems to study biointeractions [31].

Colloidal lithography is also known as nanosphere lithography (NSL), and it is characterized by its low cost, easy implementation, and parallel, high-throughput nanomanufacturing which offers the significant advantage of producing a wide variety of nanoparticles arrays in the range of 20 to 1000 nm [29].
This self-assembly procedure is based on the formation of a two-dimensional colloidal crystal deposition mask (Figure 2.2). This mask can be achieved by spin coating, drop coating or thermoelectrically cooled angle coating; the requirement is that nanospheres should freely extend on the substrate to attain their lowest energy configuration. When the solvent evaporates, capillary forces make nanospheres pack in hexagonal arrangements on top of the substrate [29].

After the crystallization of the mask, metals can be deposited onto the substrate through the mask by thermal evaporation, electron beam deposition or pulsed laser deposition until a controlled mask thickness $d_m$ is obtained. Once this step is completed, the nanospheres are removed by immersion of the sample in a solvent, and the deposited material is left on the substrate. Several structures can be obtained after deposition depending on the particle array (single layer or double layer) [29].
A variation of the aforementioned technique is to change the material deposition angle (figure 2.3). This modification is known as angle-resolved NSL. When applying AR NSL the size and shape of the nanostructures changes accordingly to the deposition angle (θ_{dep}). If the deposition angle is increased, the patterns on the substrate will decrease in size and shift from their original position. The advantage of this technique is that the nanoparticles produced can achieve sizes from 1 to 20 nm, without having to employ self assembly of nanospheres with diameters in the order of 5 to 100 nm. The problem of using those diameters in self assembled monolayers is that their arrangement is difficult due to larger polydispersity. Furthermore, if θ_{dep} is varied between two depositions, nano-overlap and nano-gap structures can be patterned [29].

2.2.3 Anodization Process

Another variation of self-assembled monolayers used for nanopatterning purposes is the anodization process. Self-organized porous alumina has been used as a mask and subsequent metal deposition through the pores of the mask has permitted
the creation of metal nanodots. Also nanoholes were created utilizing the same anodic alumina by applying a chemical etching instead of depositing metal nanoparticles [28].

![Figure 2.4 Schematic diagram of the patterning process by localized anodization of Si through anodic porous alumina as mask [28]]

First an aluminium film is sputtered on a p-type silicon substrate, and then it is anodized at a constant voltage (10-240 V depending on the pore size desired) in oxalic acid solution. After anodization, self-ordered porous alumina is obtained as well as silicon oxide dots in the conductive area between the porous film and the substrate. The next step is to remove the self ordered porous alumina. SiO₂ convex features formed during anodization over the silicon substrate are also eliminated by hydrofluoric acid (HF) etching. Finally, concave patterns similar to the porous nanopattern of anodic alumina are transferred to the substrate in the form nanoholes exhibiting the same periodicity as the former (figure 2.4) [28].

To fabricate nanodots, the same anodization process is applied through an electroless deposition of metallic particles through the porous alumina. In order to reach the SiO₂ layer below the porous alumina barrier, a through hole is made by immersing the sample in phosphoric acid. Different materials can be used for electroless deposition and consequent formation of nanodots. For example, Cu dots
can be electroless deposited on a Si substrate by utilizing a CuSO₄/HF solution which will also dissolve the SiO₂ formed during anodization of the Si substrate localized below the alumina mask. As a final step, porous alumina is removed by a chromic-phosphoric acid mixture [28].

### 2.2.4 Back-Side Irradiation

Backside-irradiation is a projection optical lithography method where feature sizes below $\lambda/260$ has been demonstrated in silicon surfaces. An infrared laser ($\lambda = 10.6 \ \mu m$) is used to irradiate the backside of a silicon substrate with Au particles on its surface (figure 2.5). This can be done because the Si substrate absorbs 80% of the CO₂ laser light and is able to transmit a fifth of the total laser energy measured. The nanopatterning mechanism in this method is attributed to localized dipolar excitations in Au colloid clusters. A disadvantage of this method is that resultant structures are not homogenous in size and density which suggest low control over these features [32].

![Figure 2.5 Schematic diagram of the Backside irradiation process [32]](image)

### 2.2.5 Proximity Field Nanopatterning

Proximity field nanopatterning (PnP) makes use of conformable phase masks to fabricate 3D nanostructures by direct conformal contact. It was proposed for the
fabrication of photonic bandgap structures at low cost and high throughput. Optical alignment of the mask depends on Van der Waals forces between the mask and the surface. It offers high tolerance to vibrations and does not need complex optical alignment setups. Moreover, energy sources of low coherence can be employed and high resolution can be attained because of its contact mode procedure [33].

Figure 2.6 (a) Schematic diagram of the PnP technique, (b) Controlled defect structure in PnP mask (top) and in a patterned 3D structure exposed at 355 nm (bottom) [33]

The masks used in PnP are made of elastomer materials like PDMS and are fabricated by soft-lithography. When the mask is in contact with a photopolymer thin film, Van der Waals forces attract the mask into close contact with the surface, without the need for applying an external force. When light is focused onto the mask
it forms a 3D intensity distribution that generates exposure of the polymer film throughout its thickness. When the mask is removed and the unexposed sections of the polymer are developed, 3D nanostructures (feature sizes ~50 nm) resembling the intensity distribution are obtained (figure 2.6). The self image formation of the structure (Talbot effect) is responsible for the electric field minima and maxima along $z$; the Talbot distance is a function of grating periodicity and incident wavelength. The size of the patterned areas is limited by the spot size of the light source and the size of the mask. 3D nanostructure thickness is constrained by the structural integrity and optical absorption of the photopolymer. Nevertheless, the PnP method offers large processing areas, high throughput and low fabrication costs. Another benefit of this technique is that it can generate aperiodic structures, point defects and varying periodicities [33].

2.2.6 Nanoimprinting

Nanoimprinting takes place through contact printing and embossing under the correct temperature and pressure. Patterns in the nanometre scale can be obtained [34]. The drawback of this method is that each original template must be made using other expensive or slow nanolithographic techniques, like deep UV and EBL lithography [35]. Other limitations include restrictions on high resolution patterns and 2D nanofabrication [30]. On the other hand, it is not affected by wave diffraction. The technique employs the following mechanism: a master is pressed into a substrate covered by a thin film of polymer resist. The process occurs at temperatures higher than the thin film resist glass transition. After several minutes, the master is released and reaction ion etching is used to remove residues left in the embossed areas [36].
2.2.7 Hot Embossing

Hot embossing technique employs moulds to nanopattern substrate surfaces. The process starts by placing the mould on top of the substrate and then collocated in a heating plate. When the temperature is above its glass transition point the substrate softens and takes the form of the mould. This method can be used to produce microlens arrays [37].

2.2.8 Micro contact Printing

Microcontact printing strongly depends on the formation of self assembled monolayers (SAMs). Long-chain alkanethiols of gold have been used to fabricate structures with “well-defined molecular thin films” [38]. SAMs are achieved by the immersion of a gold substrate into dilute solutions of alkanethiols for some hours. In contact printing, SAMs are formed in the substrate areas that are in direct contact with a rubber stamp inked with alkanethiols. During contact, the alkanethiol monolayer is transferred to the surface in just a few milliseconds due to the high local concentration of ink near the surface (figure 2.7). The purpose of utilizing SAMs is to substitute the use of photoresist films and also to enhance the possibility to control and bind chemical reactions on top of them. The main disadvantage of this technique is the spreading of the ink molecules resulting in an uncontrolled transfer and pattern distortion. In order to avoid the aforementioned difficulty, it has been suggested to employ high ink concentrations and shorter printing times (3 ms) which will enable a homogenous deposition of SAMs. To further develop the nanoimprinting method, suitable materials for the stamps and better control on ink diffusion need to be investigated if a good resolution is expected in the sub-100 nm scale. The materials of the stamp need to be hard enough to avoid pattern deformation but at the same time be soft to allow conformal contact. [38].
2.2.9 Dip-Pen Nanolithography

SAMs can also be used in a top-down nanopatterning method known as dip-pen nanolithography (DPN). In this method, nanopattern fabrication takes place by dipping an atomic force microscopy (AFM) tip into an ink containing alkanethiols and then scanning it over a gold surface. The ink molecules are attracted to the surface thanks to a capillary bridge of surface-bonded water (figure 2.8). This technique allows for higher resolution patterns than those obtained with micro/nanoimprinting. The drawbacks of DPN nanolithography include slow processing due to its direct-writing nature and small patterning areas. A proposed solution for this is to utilize multiple pens arranged as a bundle of tips, to achieve parallelization of the process, also known as 2D DPN. This modification to the DPN method does not use stamp designs or lithography steps. With 1 bundle of tips complex geometries can be written over a surface, saving time and decreasing fabrication costs [38].
2.2.10 Evanescent Near-Field Lithography

Evanescent Near-Field Lithography makes use of the evanescent optical field setup under a contact mask for exposure with resolution results of $\lambda/20$ [32]. Planar metal films can be used in order to project near-field patterns due to the special properties of surface plasmons. Surface plasmons at planar surfaces can be defined as longitudinal charge density fluctuations that take place at the boundary between a metal and a dielectric. The electromagnetic fields resulting from the SP resonance exponentially decay normal to the surface. It has been proposed that a coherent superposition of SP oscillations with different wavevectors on a metal surface will generate an image with a resolution far below the diffraction limit [39].
Evanescent near-field optical lithography (ENFOL) utilizes illumination in the range of 365 to 600 nm, and represents an extension of optical lithography to pattern in the sub-100 nm scale. It can employ ultrathin photoresist films and conformable photomasks to attain both additive and subtractive pattern processes. Its principle of operation consists of the close contact between a conformable membrane mask and a substrate with a photoresist coated on it (figure 2.9). It has to be assured that the distance between these elements is much lower than the wavelength of the light source. The optical near field in the photoresist film includes high spatial frequency evanescent components and propagating diffracted components. These components will increase the resolution of the nanopatterns below the diffraction limit imposed by conventional lithography techniques. The rigorous precision on the gap between the conformable mask and the substrate is a factor that can be controlled by external pressure or vacuum conditions [40].

One of the disadvantages of the ENFOL technique is that the photoresist thickness is one of the elements that define the resolution and quality of the patterns. Generally, a thickness of 60 nm is desired for performing exposure within the evanescent near field of the mask. If a thinner resist is used, pattern transfer is worsened when applying RIE. If a thicker resist is employed, the resolution of the pattern is not so good due to diffraction [40].

Two pattern transfer techniques are used to assure a successful sub-diffraction resolution in ultrathin resists: Subtractive (i.e. etching) and additive (i.e. lift-off process).

![Schematic diagram showing the steps in the subtractive pattern transfer using RIE](image)

**Figure 2.10** Schematic diagram showing the steps in the subtractive pattern transfer using RIE [40]
In subtractive transfer, reactive ion etching is used to remove material using the resist film as an etch mask (figure 2.10). The risk involved is that if the resist is too fine, it can be etched away along with the silicon substrate by the reactive gas.

For additive pattern transfer, a top imaging layer is included, followed by a layer which acts as a hard etch mask and an antireflection coating at the bottom of the scheme. Once the imaging layer is exposed and developed, two RIE steps are applied to remove the following masks. After etching, the lift-off stage starts by depositing different materials (e.g. NiCr) by thermal evaporation. As a final step, lift-off of the remaining layers occurs by means of a developer (figure 2.11). The additive method guarantees pattern quality and can be used to fabricate fine nanostructures [40].

![Figure 2.11 Schematic diagram of the lift-off process used with a trilayer, additive pattern-transfer](image)

An important parameter in ENFOL is the depth of field. It is defined as the depth at which there is sufficient contrast to expose the resist. It depends on the chemical composition of the resist and the exposure environment. The contrast on the image at a distance $y$ below the mask is given by [40]:

$$
\text{contrast} = \frac{I_y - I_0}{I_0}
$$
2.2.11 Photoresist Reflow Method

The photoresist reflow method has been used to fabricate microlens arrays. It consists of the melting of islands of photoresist. When this occurs, the liquid photoresist surfaces form a droplet which minimises the energy of the system. The shapes obtained resemble a spherical surface but more complex features can be formed due to the existence of physical constraints like the critical angle which is the angle at which the photoresist is in contact with the solid substrate [37].

2.2.12 Layer-By-Layer Assembly

Layer-by-layer (LbL) assembly is a nanomanufacturing technique used to fabricate novel multi-layered nanocomposite materials and structures with tailored chemical, mechanical, electrical, magnetic, thermal, and optical properties. Some of its applications are found in biocompatible coatings, nanoengineered capsules, pulp
microfibre nanocoatings and polymer-based electronic devices. This technique is a type of self-assembled system in which basic unit blocks associate to form a more complex structure having an architecture determined by the bonds and shapes of the unit elements. Another advantage of this method is the diversity of substances that can be employed as film constituents. The method is based on the resaturation of polyelectrolyte adsorption, which reverses the terminal surface charge of the film after each layer is deposited. The ultrathin multilayer films can have a precision finer than 1 nm and at the same time a well defined molecular composition [41].

![Figure 2.12](image)

**Figure 2.12** Schematic diagram of the LbL assembly by alternate adsorption of polycations and polyanions or nanoparticles [41]

The technique applied on planar solid substrates begins by a polycation solution added to a suspension of colloidal particles. When adsorption saturation occurs, separation of the particles from free polycations in the solution takes place. After this, a polyanion layer is deposited. The adsorption of alternately charged polyelectrolytes contained in solution is the basis of the process (figure 2.12). Then, water-soluble or dispersible elements having charges can be considered to build the resulting films. The initial material could be metallic, plastic, ceramic and the LbL-assembled material may consist of polymers, nanoparticles or proteins [41].
### 2.2.13 Conclusions

The aforementioned techniques although varied have provided a guide for micro/nano processing criteria, listed in table 2.1. If a technique is to be developed and implemented, this set of considerations should be taken into account in order to aid the optimisation of processing parameters.

<table>
<thead>
<tr>
<th>Desirable characteristics</th>
<th>Detrimental aspects</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Low cost</td>
<td>• Expensive processing steps</td>
</tr>
<tr>
<td>• Simple steps/alignment/implementation</td>
<td>• Expensive or numerous processing steps</td>
</tr>
<tr>
<td>• High throughput</td>
<td>• Slow processing</td>
</tr>
<tr>
<td>• Tolerance to setup vibration</td>
<td>• Rigorous precision of mask/substrate gap</td>
</tr>
<tr>
<td>• High resolution</td>
<td>• Uncontrolled pattern transfer/distortion</td>
</tr>
<tr>
<td>• Large processing areas</td>
<td>• Small patterning areas</td>
</tr>
<tr>
<td>• Generation of aperiodic structures, point defects, varying patterns/periodicity</td>
<td>• Homogeneous nature and restriction to fabricate complex features/parallel throughput</td>
</tr>
<tr>
<td>• Unaffected by wave diffraction</td>
<td></td>
</tr>
</tbody>
</table>
3.1 Laser Beam Characteristics

The acronym LASER stands for the process of Light Amplification by Stimulated Emission of Radiation. Light amplification takes place inside a resonator or cavity which comprises two mirrors, one at each end of the laser medium. While one of the mirrors is totally reflecting allowing light to bounce back and forth along the optical axis, the other mirror partially transmits some light out off the chamber (i.e. the operating beam). This constitutes the laser optical feedback system in which the outcome is often (but not always) a coherent and highly orientated beam with the following characteristics [42]:

- Wavelength: This property is inherent to the transitions taking place by stimulated emission inside the laser cavity.
- Coherence: Due to stimulated emission, radiation is a self-generating process where a continuous wave train of many meters long can be obtained. This indicates that the phase difference ($\Delta\phi$) at a single point in space measured at the beginning and end of a fixed time interval ($\Delta t$) is time-independent (perfect temporal coherence). In the same manner, the phase difference measured at any two fixed points perpendicular to light propagation is also time-independent (perfect spatial coherence) [43].
- Mode and Beam Diameter: Standing electromagnetic waves, which depend on the cavity geometry, appear as radiation oscillates. Even with small angle variations, different longitudinal standing waves may form and interfere, giving rise to a transverse standing wave. This transverse wave defines the
mode structure of the beam coming out from the cavity [42]. According to the orders of mode, Transverse Electromagnetic Mode patterns (TEM\textsubscript{plq}) can be classified as: p (number of radial zero fields), l (number of angular zero fields), and q (number of longitudinal zero fields).

### 3.2 Focal Spot Size

When a lens is used to focus a beam of finite diameter (D) towards a sample, it conducts all rays at the focal plane where constructive and destructive interference will occur. In the “Fraunhofer” Diffraction Pattern, the first dark ring appears because two rays (\(\lambda/2\) out of phase) arrive at the same point and destructive interference takes place. This results in a decrease in light intensity. In the other hand, when the rays are in phase, constructive interference appears [42]. The focussed beam diameter is known as the central maximum which is said to contain 86% of all the beam power [42]. It covers the points where light intensity has diminished to (1/e\(^2\)) of the central value. If the beam has a rectangular shape with a plane wave front, \(d_{\text{min}}\) is defined as:

\[
d_{\text{min}} = \frac{2f\lambda}{D};
\]  

(3.1)

For circular beams, a factor of 1.22 is introduced and the equation for the diffraction limited spot size changes to:

\[
d_{\text{min}} = \frac{2.44f\lambda}{D};
\]  

(3.2)

For Gaussian beams a further correction is needed: multi mode beams (TEM\textsubscript{plq}) will focus a minimum spot size accordingly to its radial and angular nulls:

\[
d_{\text{min}} = \frac{2.44f\lambda}{D}(2p+l+1);
\]  

(3.3)
3.3 Beam Quality $M^2$

Due to diffraction, a laser beam will diverge at an increasing rate from its initial waist $D_0$ until it reaches a maximum known as the far field divergence $\Theta_{\infty}$. If the beam is focused by a lens it will converge to a new waist $D_1$ and diverge again with a far field divergence of $\Theta_{\infty}$ [42]:

$$D_0 \Theta_{\infty} = D_1 \Theta_{\infty} = \text{constant} \quad (3.4)$$

The Beam Quality Factor $M^2$ compares the actual beam divergence $\Theta_{\text{act}}$ with the divergence of a Gaussian laser beam having the same initial waist $\Theta_r$:

$$M^2 = \frac{\Theta_{\text{act}}}{\Theta_r} \quad (3.5)$$

Then for a lens, the spot size can also be obtained by:

$$\Theta_{\text{act}} = \frac{D_L}{2f} \quad \text{and} \quad \Theta_r = \frac{2\lambda}{\pi d_{\text{min}}} \quad \therefore \quad d_{\text{min}} = \frac{4M^2 f\lambda}{\pi D_L} \quad (3.6)$$

Higher order mode beams can be treated as Gaussian by using the quality factor $M^2$. For example, the beam diameter $D_z$, starting from the beam waist to any point along the beam path $z$ is given by [42]:

$$D_z = D_0 \left(1 + \left(\frac{4M^2 \lambda z}{\pi D_0^2}\right)^2\right)^{1/2} \quad (3.7)$$

Furthermore, the wave front radius $R_z$ can be obtained by:

$$R_z = z \left(1 + \left(\frac{\pi D_0^2}{4M^2 \lambda z}\right)^2\right)^{1/2} \quad (3.8)$$
The distance from the beam waist where the diameter is $D_0$, to the point where it reaches $\sqrt{2}D_0$, is known as the Rayleigh Range and is related to the quality factor by [42]:

$$R = \left( \frac{\pi D_0^2}{4M^2\lambda} \right); \quad (3.9)$$

The distance where the beam spot size grows by 5% is known as the depth of focus ($z_f$) and is defined as [42]:

$$z_f = \pm 0.08\pi \frac{D_0^2}{M^2\lambda}; \quad (3.10)$$

Also, if the focussed beam converges with an angle having a tangent equal to $D/(2f)$ [42]:

$$\frac{f}{z_f} = \frac{D}{1.05d_{\text{min}}} = \frac{D}{1.05(2.44f\lambda/D)}; \quad (3.11)$$

$$z_f \pm 2.56F^2\lambda; \quad (3.12)$$

where $F = \frac{f}{D}$.

For multimode beams the depth of focus is defined as:

$$z_f = \pm 2.56F^2M^2\lambda; \quad (3.13)$$

And the spot size focussed by a lens at a distance $z$ from the beam waist can be calculated as [42]:
3.4 Laser Interferometric Lithography

Interferometric Lithography has the capability to produce periodic arrays of lines or dots over large areas. If combined with high repetition EUV lasers it is a useful tool to pattern nanoscale features by means of interference effects. An illumination source with a high degree of spatial and temporal coherence is needed in order to obtain a good interference pattern, as well as a high average of power that would allow short exposure times. In Lloyd’s mirror interferometer [43], a part of the beam impinges on a mirror at an incidence angle (θ) which is then reflected and interferes with the undeflected portion of the beam, see fig. 3.1 [44]. This interference results in an intensity pattern of period Δ, defined by the wavelength of light λ and the grazing incidence angle θ, in accordance with the grating equation:

\[
\Delta = \frac{\lambda}{2 \sin(\theta)}; \quad (3.15)
\]

\[
d_{\text{min}} = \frac{4fM^2\lambda}{\pi D_z}; \quad (3.14)
\]
When two planar waves of coherent light interfere, the resultant pattern of parallel fringes can be used to expose a photosensitive film. Moreover, a double-exposure method can form a mesh pattern just by rotating the substrate over 90 degrees after the first exposure. Gratings crossing each other are obtained, and by development of the photoresist, a square array of pores is generated (fig. 3.2) [45].

![Figure 3.2 Schematic illustration of: (a) First exposure of the substrate, (b) 90 degrees rotation of the substrate, (c) Second exposure [45]](image)

It is important to consider the characteristic penetration depth in the material used for interferometric lithography. If it is too small, a low vertical modulation of the pattern on developed resists can arise which is not convenient. To avoid undesirable results, parameters like resist composition and thickness, development procedure and illumination dose have to be optimized [24].

Multiple beam laser interference lithography has several drawbacks like complex experimental setup which requires high coherence laser sources, vibration isolation and bulk optics (e.g. beamsplitters, mirrors and delay stages) [33]. On the other hand, if a single pulse irradiation is used, a vibration isolation table is not necessary and the quality of the nanostructures is improved. To avoid excessive spatial and temporal deviation of two beams and consequently improve the modulation profile of high resolution grating, the laser must be spatially collimated and the interferometric system must be precisely assembled [46].

An application of the two-beam interference ablation technique is the manufacturing of high resolution gratings to be used in optical waveguide devices and Bragg
reflectors. Diffraction efficiencies of 55.4% have been measured for relief gratings. The gratings can be transferred to a UV curable epoxy resin in order to obtain an embossing master for massive fabrication [46].

### 3.4.1 Fibre Bragg Gratings

Fibre Bragg gratings (FBG) are embedded within a material to monitor the real time condition of some factors like the load, strain, temperature or vibration. They usually are holographically written into Ge doped fibres by exposure to UV interference. As a result, a grating showing periodic modulation of the refractive index in the fibre core reflects light of wavelength $\lambda$, satisfying the Bragg condition $\lambda_B = 2n_{\text{eff}} \Lambda$ where $n_{\text{eff}}$ is the effective mode refractive index and $\Lambda$, the grating period. This period is strongly affected by the temperature or the strain of the fibre so, by evaluating the shift in the reflected wavelength, these factors can be measured [47].

Considering the external parameter to be sensed (e.g. temperature ($T$), strain ($\varepsilon$), hydrostatic pressure ($P$), or refractive index of the cladding ($n_{\text{cl}}$)) to be $X$, the shift in Bragg wavelength can be calculated as follows [48]:

$$\begin{align*}
\bar{\lambda}_B &= 2n_{\text{eff}} \Lambda; \\
\frac{d\bar{\lambda}_B}{dX} &= 2 \frac{d}{dX} \left( n_{\text{eff}} \Lambda \right) = 2 \Lambda \frac{dn_{\text{eff}}}{dX} + 2n_{\text{eff}} \frac{d\Lambda}{dX} = 2\Lambda \frac{\Delta n_{\text{eff}}}{n_{\text{eff}}} + 2n_{\text{eff}} \Lambda \alpha; \quad (3.16) \\
\frac{1}{\bar{\lambda}_B} \frac{d\bar{\lambda}_B}{dX} &= \frac{2\Lambda \Delta n_{\text{eff}}}{2n_{\text{eff}} \Lambda} + \frac{2n_{\text{eff}} \Lambda \alpha}{2n_{\text{eff}} \Lambda} = \frac{\Delta n_{\text{eff}}}{n_{\text{eff}}} + \alpha; \\
\Delta \lambda_B &= \frac{d\bar{\lambda}_B}{dX} \Delta X = \lambda_B \left( \frac{\Delta n_{\text{eff}}}{n_{\text{eff}}} + \alpha \right) \Delta X; \quad (3.17)
\end{align*}$$

Where $\Delta n_{\text{eff}}/n_{\text{eff}}$ is the normalised sensitivity of the effective mode refractive index, and $\alpha$ is the coefficient of physical length change dependent on the parameter $X$. In this manner, for a temperature change the normalised sensitivity of the effective mode index is known as the thermally induced refractive index change or thermo-
optic coefficient \([49] \left( \xi = 1/n_{\text{eff}} \right) \text{d}n_{\text{eff}}/\text{dT} \), and \( \alpha \) is the thermal expansion coefficient. Combining these two parameters the shift in Bragg wavelength due to a change in temperature can be calculated as:

\[
\Delta \lambda_b(T) = \lambda_b \left( \xi + \alpha \right) \Delta T; \quad (3.18)
\]

Strain measurements can be obtained by employing the equation:

\[
\Delta \lambda_b(T) = \lambda_b \left( 1 - \rho_a \right) \varepsilon; \quad (3.19)
\]

\[
\rho_a = \frac{n_{\text{eff}}^2}{2} \left[ \rho_{12} - \sigma (\rho_{11} - \rho_{12}) \right]; \quad (3.20)
\]

Where \( \rho_a \) is the stress-optic coefficient and \( \rho_{12} \) and \( \rho_{11} \) are coefficients of the stress-optic tensor, and \( \sigma \) is Poisson’s ratio. In the case of isotropic and homogenous strain:

\[
\Delta \lambda_b(T) = \lambda_b \left( 1 - P_e \right) \varepsilon; \quad (3.21)
\]

Where \( P_e \) is the strain-optic coefficient.

### 3.4.2 Microlens Arrays

Another application is the fabrication of microlens arrays (MLAs) which are constructed by a series of miniaturized lenses with a certain arrangement. A microlens array can focus the light into an array of small spots to be applied in micro and nanolithography.

The MLA technique can be used to nanopattern phase change materials by employing a femtosecond laser as the light source. Its nanopatterning mechanism is based on a photochemical reaction under UV laser irradiation. When the laser fluence is raised, the pattern size increases because more photon energy is absorbed by the photopolymer. Axial sizes in the sub-200 nm range are obtained with lens diameters of 23 micrometers. Attention must be paid to the distance between the
MLA and the surface because a non uniform placement of the array above the substrate can provoke different focal points. This last can be achieved by means of a high resolution nanostage and a MLA alignment system [50].

3.5 Laser-Induced Forward Transfer

Laser induced forward transfer (LIFT) technique is a nanofabrication method that has been employed for the fabrication of carbon nanotube patterns. It is also utilised for deposition of metallic films on substrates. By laser irradiation, the film (previously precoated over a transparent material) is transferred onto a surface by single laser pulses. It has to be considered that the transparent material has to be brought in close proximity with the substrate; this can contain a mask with predefined patterns. When the precoated material absorbs the laser energy, it evaporates and is subsequently deposited on the substrate through patterned orifices on the mask. As a last step, the mask is removed from the substrate (figure 3.4) [51].

![Figure 3.3](image)

**Figure 3.3** Schematic diagram of pattern deposition of a carbon nanotube film by laser transfer method [51]

3.6 Laser-Induced Plasma Assisted Ablation

In laser-induced plasma assisted ablation (LIPAA), the generation of plasma is given by the adsorption of laser light by the medium. This plasma is able to ablate
in a very precise way hard materials like SiC. Another example of hybrid laser processing is the Contact Particle-Lens Array (CPLA) technique. It employs an enhanced electromagnetic field to make nanopatterns, by utilizing a mask of spherical nanoparticles [52]. This near-field phenomenon will be explained in the following section.

3.7 Near-Field Patterning Techniques

Near field patterning techniques are based on near field optics. These techniques have become widely studied because they can deliver high resolution below the diffraction limit of light without the need for complex and expensive systems such as those employed for electron beam lithography (EBL) or focused ion beam (FIB) lithography.

3.7.1 Non-Resonant Near-Field Optical Chemical Vapour Deposition

Non-resonant Near-Field Optical Chemical Vapour Deposition provides excellent spatial resolution, accurate control of size and position and can be applied by the means of different metals (e.g. Zn, Al). Deposition can achieve a precision of approximately 1 nm. The setup for this technique utilizes a buffer gas (e.g. ultra high purity argon) and a reacting molecular gas source (e.g. diethylzinc DEZn). Also, it includes a laser (as the light source) and a fibre probe, in which an optical near field is generated at its apex. This optical near field is the mechanism responsible for photo-dissociation and deposition of the reactive molecular gas (figure 3.5) [6].
3.7.2 Laser irradiation in conjugation with scanning probe microscopy

Laser irradiation can be combined with Scanning Probe Microscopy (SPM) to nanopattern structures in the sub-100 nm scale. The laser beam is focused between the SPM apex and the surface. Then the tip scans over the top of the substrate, which can be a metal or a photoresist, obtaining high resolution nanolines and nanocharacters. Careful attention must be paid to the laser processing parameters in order to achieve extended control over depth and width of nanostructures. The advantages of this type of laser processing are its easy setup, fast speed and large nanopatterned areas. The setup can be realized in open air with a commercial scanning probe microscopy system. The laser fluence used during the process has to be set at a value lower than the ablation threshold for the tip and the substrate in order to avoid their damage. Additionally, the sample position can be controlled via a tube scanner (figure 3.6) [53].
Two possible mechanisms can explain laser nanopatterning using a SPM tip. The first one relates to the thermal expansion given by the laser energy absorbed by the tip and the substrate. In the second one, the SPM tip is seen as an “antenna”. By this effect, the electric field localized under the tip is enhanced and is responsible for the ejection of surface materials and the consequent formation of nanostructures. Both mechanisms depend on tip sharpness, scanning speed, scanning times and laser fluence, to achieve variation in depth and width of the nanopatterns. For example, it has been demonstrated, that with increased laser fluence, depth and width are also augmented. Depth can be increased if the scanning speed is lowered, the sample is scanned more than once and the laser fluence is increased. Width can be decreased if a lower laser fluence is set for the process and also if the scan speed is increased. This technique is flexible enough to provide a wide range of nanopatterns by software programming of the scanning path. Besides, if reactive ion etching (RIE) is applied after the nanoprocessing, different nanodevices (e.g. NEMS structures) can be created [53].

3.7.3 Near-field optical microscope patterning

One of the most used near-field techniques is that of near-field optical microscope (NSOM) patterning. In this method, the separation between the aperture
and the surface is small compared to the wavelength, and the resolution obtained in the medium is given by the size of the aperture rather than by the diffraction limit. In the NSOM system the light source is coupled to a single hollow optical fibre with a small aperture at its end. The near-field enhancement localized at the tip of the NSOM is the mechanism responsible for the nanopatterning of the substrate material [54]. Moving the piezo stage in which the sample is mounted while laser light is irradiated through the nanotip makes possible the design of complex structures [55].

The noncontact mode of this method is based on the vibration of the nanoprobe at its resonance frequency using a PZT-actuating-endcap and a lock-in amplifier. This mode (non contact) is employed when the surface material is soft, because the pattern width in contact mode is barely larger due to a stronger near-field coupling [55]. It has to be noted that the main factor responsible for pattern width is the total amount of energy irradiated on the surface. As it increases, the bulk of photochemically reacted material expands from the focusing spot making the pattern wider and deeper. The width of nanopatterns decreases with low laser power and faster scan speeds. Care must be taken when applying this technique to nanopatterning of substrates (silicon wafers) because the depth of the nanostructures has to be large enough to account for the etching processes. One way of doing this is to increase the scanning times but attention is to be paid because the width will also increase and deteriorate the spatial resolution. However, a good way to compensate for this will be to reduce the thickness of the photoresist [27].

Benefits from NSOM nanopatterning include the fact that it is done in air and is maskless, permitting flexible changes in the fabricated designs [27]. One of the disadvantages of this technique is that it cannot be scaled to an industrial environment because of its low throughput and a strict control of the near-field distance. Because of the small aperture of the probe, large areas cannot be processed within short periods of time so it has been proposed to employ multiple nanopores in the form of parallel-type cantilever nanopores in order to enhance productivity [55].
NSOM-based techniques are applied depending on three different nanofabrication purposes: material modification, material addition and material removal. NSOM is defined as a probe technology that optically alters materials at spatial resolutions beyond the diffraction limit of light. One of the advantages of NSOM technology over scanning tunneling microscope (STM) is that the sample used can be non-conductive. This is because NSOM detects the tunneling of photons rather than the electron tunneling currents, sensed in STM. Another benefit of NSOM technology is that it can employ diverse energy sources like electrostatic, optical, optochemical, optoelectrical, optomagnetic and thermal [56].

Two types of probes can be used in NSOM: with aperture and apertureless. The advantage of a probe having an aperture is that light irradiation can be controlled directly and a wider range of materials is available (figure 3.7) [55].

The aperture of a NSOM system is fabricated by tapering an optic fiber to a sharpen tip and then applying a metal coating to the entire fiber but without covering the tip. The metal coating will enhance resolution due to a better confinement of light. While the probe is maintained in close contact with the sample, the evanescent field exiting the probe aperture illuminates the sample. Excited atoms in the sample re-radiate propagating waves, enabling the probe to collect those propagating waves for their further transmission to a photodetector [56].

By using aperture NSOM probes, light is confined to a certain resolution dictated by the size of the aperture. When an apertureless probe is employed this limitation is overcome because a sharper tip scans the surface in the near field. To achieve this, far field light is directed to the sample to produce an evanescent field over the surface. The atoms in the tip are excited (due to the evanescent photons), and re-radiate the propagating photons [56].
Material modification by NSOM relies on the use of the probe as a source energy to modify materials like photoresists, electro-magneto-optical materials, ferroelectrics and self-assembled monolayers (SAM). An aperture probe is used to scan the materials surface by confining the lateral dimension of light in the sub-wavelength scale. When localized in close proximity to the surface, the optical near field is the mechanism that patterns the area because at this distance light waves do not propagate but decay exponentially perpendicular to the surface [56].

An application of material modification by NSOM is found in the data storage industry. An array of 60 nm bits has been reported on a GeSbTe film. Due to the increased temperature given by the irradiated light through the probe, a change of phase in the film occurred from amorphous to crystalline, affecting the local reflectivity of the film and preparing it for readout in reflection mode [56].

Also a probe-based thermomechanical data storage system known as the “Millipede” has been proven successful with initial areal densities of 100 to 200 Gb/in$^2$ by utilizing a 32x32 cantilever/tip array. For the writing process, a local force has to be applied by the cantilever/tip to the polymer. Then, softening of the material occurs by heating and an indentation is made. In order to read the data bit indentation, a change of resistance in the film is detected by scanning the
cantilever/tip over the surface. Some of the factors that have to be improved in the “Millipede System” are uniformity of the cantilever/tip arrays, system reliability, and data rates [57].

Material removal by NSOM refers to the photon energy utilized to chemically etch material. It can also be seen as a mechanism to physically ablate material. One example of the first function is laser-induced chemical etching. Results of this process are attributed to photophysical phenomena and not to thermal ablation. Ablation needs a higher amount of energy than the normally employed in assisted etching. The energy transmitted ejects atoms and molecules from the surface. This mechanism is known as photothermal dominated ablation. Important factors to be considered are the use of a laser with shorter wavelength and absorbance of materials at such wavelength. The material removal function could be used to repair lithographic masks. Femtosecond lasers possess a multiphoton absorption mechanism which makes them suitable for modification of transparent materials like quartz substrates used in the masks [56].

Material addition by NSOM is performed by using the probe tip as a near field light source. This source provides a photocurrent that induces electrochemical reduction of metallic ions. This electrochemical process prompts material deposition over the surface. Another NSOM deposition technique includes chemical vapour deposition (CVD), in which a precursor gas is photodissociated by the second harmonic of an Ar laser. The height of the deposited nanostructures can be adjusted by the irradiation time and the increase in the input of the near field energy; the lateral dimension is resolved by the aperture size [56].

The nanolithographic resolution in NSOM is limited by the tip opening but this is also constrained by the amount of light that can pass through it. Moreover, the input power cannot be raised too high because it will damage the coating. For these reasons, apertureless NSOM was developed. It is based on the effect of the local field enhancement given when a metal tip is illuminated by a laser beam. This enhancement makes the electric field become stronger by at least three orders of magnitude [56].
The light allowed in the sample corresponds to the waves propagating with constant amplitude between the probe and the surface. The imaginary part of the wave vector is related to the exponential decay of the waves within distances of the order of the wavelength. These are the evanescent waves responsible for producing the forbidden light in the sample. So the electrical field distribution of the fundamental wave is composed by the different contributions of the allowed light and the forbidden light. It has to be mentioned that the allowed light is localized at the centre of the tip and as the gap width between it and the sample is increased, the field intensity of the forbidden light decreases while the field intensity of the allowed light dominates. On the other hand, when the probe is situated closer to the surface, the intensity of the forbidden light dominates. The overall field intensity decreases with the probe-sample distance having a typical decay length similar to the tip size (approximately 50 nm). When the probe-sample distance is larger than the probe tip (50 nm) the main contributor to the total field intensity is the allowed light. An important aspect that has to be considered is that the allowed light only carries information related to the low spatial frequencies, so the probe to sample distance has to be monitored in order to detect the forbidden light which is essential to improve the resolution when the imaging mode is used in NSOM [2].

3.7.4 **Contact Particle-Lens Array**

In Contact Particle-Lens Array (CPLA) patterning, the particle mask consists of a self-arranged monolayer which offers massively parallel nanostructuring with a significant improvement in patterning speed under single laser pulse radiation [54]. Transparent spherical particles which compose the monolayer are used as lenses for focusing laser radiation. The electromagnetic field scattered by these spherical particles is described by the Mie theory. The near-field lens produces a strong field enhancement just below the contact area between the particle and the surface. The energy flux at this point is below the diffraction limit [54]. This near field enhancement is given because the gap between particle mask and substrate is much smaller than the light wavelength and also the particle diameter is smaller or in the
same order of the light wavelength. These circumstances lead to what is recognized as the optical resonance effect in the near field which is different from the sphere lens focusing in the far field [53].

Geometrical optics provides a simple approach to estimate the intensity enhancement factor under the particle [58]:

\[
\frac{I_m}{I_0} \approx \frac{a^2}{w_g^2} \approx \frac{27n^4}{(4-n^2)^3};
\]

(3.22)

Where \(a\) is the particle radius and \(a >> \lambda\), \(w_g\) is the spot size on the substrate given by: 
\[
w_g \approx a \sin^2 \theta_{om} \sin^2 \theta_{om} \sin^2 \theta_{om} = \frac{(4-n^2)^3}{(27n^4)},
\]
and \(n\) is the refractive index of the particle. It is interesting to note that both diffraction and aberration make the structure of the field more complex than that explained by geometric optics. Previous experiments have shown that the field enhancement under the particle is responsible for material modification of the substrate and even ablation can take place within a range of 100 nm. However, Mie theory is not enough to explain this mechanism because it neglects the secondary scattering of radiation, reflected from the surface. This originates from the effect of increased optical enhancement and sharpened area of field localization due to the fact that the substrate surface acts like a mirror in conjunction with the particle which can be seen as a spherical resonator. The nanostructures produced are formed at normal irradiation and in the positions where the spheres were initially located (figure 3.8) [54].

The adhesion forces responsible for attracting the particles to the substrate surface are the Van der Waals forces. On the other hand, the forces used to remove the particle from the substrate are known as laser-induced particle removal forces and owe their behaviour to the thermoelastic effect between substrate and particle. When the laser irradiates over the particle mask and the substrate, these absorb energy and due to the thermoelastic effect the particles are expelled from the surface. Also some stresses and strains appear on the surface because of the temperature increase during the process, contributing to particle removal. So, if the laser fluence is raised, particles get removed because of the substrate thermal expansion [54].
If metallic nanoparticles are used in the monolayer for nanopatterning, an outward energy flux is localized in the near-field. Surface plasmons generated in the particle due to the incident light create an enhanced field in its surface allowing nanopatterning [59]. The plasmon enhanced near-field printing process employs a mask formed by metal particles that can be put into close contact with a thin photoresist layer. Afterwards, the resist is illuminated with p-polarized light at the plasmon resonance frequency of the particles. The enhanced optical field around the metal particles causes an increased exposure of the resist layer below the particles. When the resist is developed, only the exposed areas subjected to the local field enhancement will be affected. Depending on the required resonance wavelength, (chosen according to the resist sensitivity), a certain particle material can be utilized. It has to be considered the following: if large particles are selected, the field enhancement will drop because of the excitation of multipolar oscillations inside the particles. So a proper diameter will be in the order of $0.1\lambda$ or below it [39]. It has been suggested that large nanoparticles (e.g. 1000 and 2000 nm) act as lenses and that small nanoparticles (in the submicron nanometre scale) represent a source of

![Figure 3.7 SEM images (scale bar is 1.0 µm) of nanodent structures formed on GeSbTe film under the removed particles after one laser pulse irradiation at different incidence angles: (a) 0°, (b) 30°, (c) 45° and (d) 60°; Laser fluence is 7.5 mJ/cm² [54]]
near field in which the electric field around the nanoparticles increases due to light irradiation [60].

Nanofabrication by means of this technique can take place at low energy without ablation. The explanation for this is that the irradiated intensity over the particles is enough to soften the surface by an augmentation in the temperature of the film which consequently leads to the material deformation caused by the scattering force. On the other hand, the ablation mechanism depends on a photochemical and a photothermal reaction. The photochemical reaction alone cannot ablate because the photon energy is too low to break the chemical bonds directly. So in order for ablation to occur, both reactions must be present [60].

When similar particles are situated close to each other, the energy flux is coupled allowing nanoparticle chain waveguides. But this coupling of the plasmon nanoparticles with a surface has not been investigated enough [59]. Another consideration to be made about this coupling is that it modifies the optical properties of the system resulting in an electromagnetic field distribution different to that obtained with an isolated particle. The resulting optical spectra of two adjacent nanoparticles resemble the spectra of an ellipsoid. This spectrum is expressed by the two resonant frequencies of the longitudinal and transverse modes respectively. Also it has been shown that the particle arrangements influence the electric field distribution and the enhancement factor. The highest enhancement occurs when the polarization of light is parallel to the axis of a pair of particles also known as the longitudinal mode [61].

The finite difference time domain method can be used to calculate the electric field distribution and the optical near field intensity localized under a particle placed onto a surface. This method is based on a numerical algorithm that solves Maxwell’s equations and presents the solution of electromagnetic distributions of complex geometries and inhomogenous materials [61]. Another method that can be employed is the multiple-multipole (MMP) model which incorporates a purely analytical and a purely numerical approach and can be applied to solve Maxwell’s equations for arbitrarily shaped, isotropic and linear homogenous material [2].
Recent modifications to the technique include using an angular scanning laser beam, which irradiates the mask and as a result, parallel writing of complex array patterns is obtained over a large surface area (figure 3.9) [62].

Figure 3.8 Schematic diagram of direct laser writing of nanoline array on substrate [62]

When the incidence angle is normal to the surface, most particles are removed. This occurs because the thermal deformation and/or ablative forces exceed the Van der Waals forces responsible for maintaining the particles attached to the surface. It has been demonstrated that at low laser fluences and small incident angles, the particles are not removed from the surface and because of this condition, multi-angle processing can take place. Multi-angle processing is of important relevance because it can produce continuous lines on a substrate. The characteristic length of a nanoline is given by [62]:

$$L \equiv r |\tan(\alpha_1) - \tan(\alpha_2)|$$  \hspace{1cm} (3.23)

Where $\alpha$ is the incidence angle. In order to fabricate nanolines with the same depth, the laser fluence must be varied or multiple laser pulses should be used at each different angle. In the same manner, lateral dimension uniformity can be achieved if an appropriate laser fluence is selected. This technique is not restricted to nanolines
only but complex shapes can be patterned by means of the design of the scanning path design. If CPLA patterning is combined with the use of a femtosecond laser as the light source, resolution can be greatly improved (in the order of sub-50-nm scale) [62]. Although laser parameters strongly affect surface patterning, the particle size and the light wavelength should also be monitored to achieve better control of the process [53].

If a quartz plate is placed on the sample surface (e.g. aluminium substrate) in order to fasten the self-assembled nanoparticle monolayer, two mechanisms are found responsible for the formation of the nanostructures. These are the near-field optical enhancement and the nanoimprinting processes. Near-field optical enhancement occurs when the laser fluence is very low and only the main lobe of the intensity enhancement reaches the melting point of the substrate due to optical resonance inside the particle. In this way, small holes are created on the surface. If the laser fluence is very high, the whole substrate surface is heated above the melting point because of the large amount of energy irradiated on the sample. If this is the case, the nanoimprinting mechanism takes place as the melting depth increases with the laser intensity. If the quartz plate is covering the particles, these get imprinted on the melted surface during the laser pulse and hemispherical cavities are formed due to the spherical shape of the particles. During the embossing of the silica particles on the surface, the molten material is raised. When the imprinting mechanism is dominant, the effect of the main and side lobes of the intensity enhancement disappear [63].

It has been found that the electric field can be greatly enhanced compared to the incident wave after the light travels through the micro-particle. The time averaged relationship between light intensity and the magnitude of the electric field is given by [63]:

$$I = \frac{1}{2} c \varepsilon_0 E^2$$  \hspace{1cm} (3.24)

Where $\varepsilon_0$ is the vacuum permittivity constant and $E$ is the electric field of incident light. Considering the above formula, light intensity increases with respect
to the incident wave and is confined to a small region near the contact point between the particle and the substrate surface [63].

Another modification of the CPLA technique is to employ masks manufactured by EBL or FIB techniques on quartz substrate. The limitation of this is the precision that has to be maintained between the mask and the substrate (approximately 10 nm), which can be solved by the use of scanning probe microscopy (SPM). The use of a semi-spherical/cylindrical prefabricated mask will permit the patterning of more complex geometries. By employing a laser source over the mask, laser pulsed irradiation modifies the substrate material under the mask by photochemical phenomena [53].

### 3.7.5 Femtosecond laser irradiation

Femtosecond laser irradiation provides extremely high peak power intensity for nonlinear and multiphoton absorption. This nonlinear absorption produces an increase in the refractive index at the focal point inside materials like the glass which allows for the production of nanopatterns with no cracks at the surface. If this type of irradiation is combined with a particle mask, nanoholes can be created with edges free of cracks due to the ultrashort laser pulses. Femtosecond lasers machine with minimal heat generation and the heat affected zone (HAZ) is reduced because of the short pulse durations. In this way, thermally induced substrate cracking is avoided [64]. Besides crack-free surfaces, nanopatterning quality is increased in the sense that molten material accumulation around the nanopatterns is considerably reduced. This condition is fulfilled because pulse duration is shorter than the time it takes to transfer absorbed laser energy to the lattices [53].

Laser ablation by a femtosecond laser can be distinguished by two domains regarding laser fluence. For example, on Si surfaces, laser fluences below a wavelength dependent threshold of 2 J/cm$^2$ proportionate ablation rates that are strongly dependent on the optical penetration depth. The profiles obtained under this
domain match the incident light intensity distribution. Above such a laser fluence threshold, explosive boiling could affect the underlying profiles [61].

3.8 Conclusion

The laser-based techniques documented in this review show that laser sources can be employed very effectively to pattern a variety of substrates at the micro and nano scale. Their main advantages over other micro/nano fabrication techniques include: simple processing steps, high resolution patterning, high throughput, lower costs (compared to EBL, FIB, and X-ray lithography), maskless setups, and large processing areas. These features will be further investigated and demonstrated in the next chapters.
CHAPTER 4

EXPERIMENTAL APPARATUS AND ANALYTIC EQUIPMENT

4.1 Laser Sources

4.1.1 Frequency Doubled Diode Pumped Solid State (DPSS) Nd:YVO₄ Laser

A Laservall Violino green marker system with the following characteristics was employed in this research work [65]:

- Wavelength: 532 nm
- Pulse duration: 8ns
- Nominal Maximum Average Power: 7 Watts
- Laser Mode: TEM₀₀
- Beam Quality: M² < 1.2
- Repetition rate: 20 kHz - 100 kHz

Figure 4.1 DPSS Nd:YVO₄ laser system (a) lay-out [65]; (b) enclosure.
The system lay-out is presented in figure 4.1. The laser diode pump module is coupled into the head resonator through a fibre optic cable. Optical efficiency conversion from pump light into laser light is 50%. The laser light is delivered to the sample surface by means of a galvo-scanner head with a focusing lens with nominal focal length of 150 mm and spot diameter of 50 µm.

A frequency doubling module brings the wavelength from 1064 nm to 532 nm and using the same focal length, the spot size can be reduced by 50%, increasing the power density and producing finer structuring. It also causes less mechanical heat stress without disrupting the ablation process [65].

### 4.1.2 ND:YAG Diode Pumped Solid State Laser (DPSS)

A commercial diode pumped Nd:YAG Laser Zone Texture (LZT) system (λ: 1064 nm, τ: 82 ns) was also utilised for the experimental work with NiP/Al disks [66]:

- Wavelength: 1064 nm
- Pulse duration: 82 ns
- Nominal Maximum Average Power: 8 Watts
- Laser Mode: TEM\(_{00}\)
- Beam Quality: M\(^2\): 1.04
- Repetition rate: 300 kHz

This system is able to commercially produce bumps on NiP/Al disks with sub-nano meter accuracy and long term stability. These bumps can achieve 6-8.5 ± 0.4 nm heights, with a circumferential pitch of 16 µm (±1 µm) and radial pitch of 16 µm (±1 µm) [66].

With a beam quality factor (M\(^2\)) of 1.04 and a beam diameter of 7 mm before focusing the beam onto the target by a single element lens (f = 50 mm), the calculated focused spot size on the disk is 10 µm. See figure 4.2 for optical lay out. A
variable attenuator was used to control the laser fluence (pulse energy per spot area) delivered to the substrate.

Figure 4.2 Laser Precision Solutions Pte LZT system (Courtesy of Precision Laser Solutions Pte Ltd) [66]
4.1.3 Femtosecond Laser system

Irradiation by femtosecond pulses was carried out by means of a Libra-S System which consists of an industrial oscillator and Regenerative Amplifier (Chirped Pulse Amplification CPA). The system comprises 5 modules [67]:

- Seed laser (Vittesse): CW DPSS laser and mode-locked Ti:Sapphire oscillator (tunable $\lambda$: 795 – 805 nm, $\tau$: < 100 fs, output power: > 1Watt)
- Ti:Sapphire Regenerative Amplifier (RA)
- Stretcher/Compressor
- DAC electronics interface module

The output characteristics of the Libra-system are listed as follows[67]:

- Nominal Maximum Average Power: 1Watt
- Repetition rate: 1 kHz
- Pulse width: < 100 fs
- Energy per pulse: > 1 mJ
- Wavelength range: 780 – 820 nm
- Beam diameter: 6 mm
The schematic of the optical set-up for the Libra-S system is shown in figure 4.3. The beam coming out from the laser enclosure is directed through a set of mirrors and passed through a neutral density filter wheel which allows for power attenuation. The beam is finally coupled into a scanning galvo-head which allows for a precise scanning path through a laser/scanner control software (WaveRunner Nutfield Technology, Inc).

The basic principle of Chirped Pulse Amplification employed by the Libra-S System is based on the generation of a very short duration pulse ($\tau$: fs, $E$: nJ, $P_{\text{peak}}$: kW) from the seed laser which is then stretched (10 000X) in order to reduce its peak power ($\tau$: ps, $E$: nJ, $P_{\text{peak}}$:W). Such a low-brightness pulse is then amplified ($\tau$: ps, $E$: µJ, $P_{\text{peak}}$:kW) as it is multi-passed through a single Ti:Sapphire laser rod. This rod is optically excited by a pulse from the frequency doubled Q-switched Nd:YLF laser. The pulse is then recompressed by means of a single diffraction grating to its original pulse duration ($\tau$: fs, $E$: µJ, $P_{\text{peak}}$:GW), see fig 4.4 [67].
4.2 Surface Characterization

4.2.1 Optical Microscope

Samples with features at the micro-scale were analysed via optical microscopy. This was performed with a Polyvar MET microscope equipped with a 100 W low-voltage halogen lamp and a 6X Objective nosepiece with magnifications ranging from 2X up to 100X. A CCD camera collected and transferred the magnified images into computer software (i-Solution DT, Image & Microscope Technology IMT).

4.2.2 White Light Optical Interferometer

3D Optical profiling of surface structures of nanometre height was realised by a high vertical resolution (> 0.1 nm), non-contact white light interferometer (VEECO Wyko NT1100) and its analytical software Wyko Vision 32. Measurement modes utilised in the present research included both: optical Phase-Shifting (PSI) and white light Vertical Scanning Interferometry (VSI). Objectives used were 5X and 50X, and for the FOV lenses: 0.5X, 1X, and 2X.
4.2.3 Scanning Electron Microscope (SEM)

A Hitachi High Technologies (S-3400N) SEM (shown in figure 4.5) offered high lateral resolution for imaging at the nanoscale, which could not be achieved through conventional microscopy due to its optical diffraction limit. Its operation principle originates from a beam of electrons scanned over the sample. As the first atomic layer of the surface reacts to such a high-energy electron bombardment, signal (e.g. secondary emission (SE) or backscattered emission (BSE) containing information about the sample’s morphology and composition is emitted and collected. Some of the main characteristics of this analytical equipment are [68]:

- High SE resolution: 3 nm (30 kV) and 10 nm at 3 kV
- High BSE resolution: 4 nm at 30 kV
- Magnification: 5X to 300,000X
- Accelerating voltage: 0.3 to 30 kV
- Electron gun: Tungsten emitter

![Figure 4.5 Hitachi High Technologies (S-3400N) SEM.](image)

4.2.4 Atomic Force Microscope (AFM)

3D Characterization of surfaces with lateral and vertical dimensions at the nanoscale was accomplished by a Veeco diInnova AFM (see fig. 4.6).
Two main measuring modes can be used: Contact and Tapping. In the first one, the probe tip interacts with the sample in permanent direct contact. During scanning the probe is submitted to a contact force which deflects the cantilever position in the Z-direction. A closed-loop feedback mechanism retrieves information from the surface’s topography by reading the laser light reflection from the top of the probe through a fibre optic interferometer. As the contact force bends the cantilever, the output signal from the feedback mechanism keeps a constant cantilever deflection in the Z-direction. In tapping mode, the probe is intermittent contact with the sample by means of an oscillating probe tip. The oscillation amplitude varies accordingly with the surface’s topography and the measurement of this variation serves as the input in the closed loop Z-feedback mechanism, which is closed by minimising this oscillation changes [69]. Data acquisition and analysis was performed with SPMLab.

Contact mode is preferred when the sample material is rigid enough to withstand the presence of lateral forces. On the other hand, tapping mode can offer high resolution topographic characterisation of soft samples (i.e. easily-damaged materials) and minimisation of effects related to friction, adhesion and electrostatic forces commonly found when the tip is in continuous contact with the sample.
4.3 Optical Properties Characterization
4.3.1 Total Surface Reflectance (Analytik Jena, SPECORD 250)

An Analytik Jena SPECORD 250 spectrophotometer with integrating sphere was used to perform total reflectance (specular and diffuse) measurements in the spectral range from 380 to 1100 nm. This type of accessory allows for accurate reflection measurements from surface structures, as the sample is brought in direct contact with the sphere becoming a part of the inner sphere surface. This inherently alters the sphere’s efficiency depending on the reflectance properties of the sample which results in the measured signal [70].

By placing the sample against the integrating sphere, the incident beam can be diffusely transmitted (sample is positioned in front of the sphere) or reflected (sample is positioned behind the sphere) into the internal reflective surface of the sphere until it reaches the detectors [71]. Total reflectance measurements are possible if a white Spectralon® insert is placed at the specular reflectance angle instead of a specular gloss trap (see fig. 4.7).

![Diagram of optical path inside the integrating sphere](image)

**Figure 4.7** Optical path inside the integrating sphere for total reflectance measurements [70]
The measurement geometry of the sphere is 8°/d (d: diffuse), so that the incident angle is 8° with respect to the surface normal. The reflectance of the sample is then defined as the radiation reflected from the sample and the radiation reflected from a matt white standard [70].

**4.3.2 Relative Reflectivity (HR4000CG Ocean Optics)**

An HR4000CG-UV-NIR Ocean Optics high-resolution (0.75 FWHM) fibre-optic spectrometer was utilised to measure relative reflectivity in the spectral range from 200 to 1100 nm. It was connected to a computer via the USB port and could be controlled through *SpectraSuite* software. Light from a halogen lamp is transmitted through a reflection probe with 6 optical fibres for illuminations. Light interacts with the sample and is then collected via the central fibre in the reflection probe. This spectral information is sent to the spectrometer which measures the amount of light and digitalises the outcome. This is then processed by *SpectraSuite* which compares it to a reference and displays the measured spectra [72].
The demand for efficient, renewable energy is a growing and crucial issue in today’s world. Solar energy offers a vast, inexhaustible, free and clean option for future power needs. Although new technologies emerge every day, silicon-based solar panels represent the most feasible and commercial solution. The reason for this is its well established manufacturing process and the abundance of this material in the earth’s crust. In order to achieve highly efficient devices, all losses associated with the photovoltaic cell operation must be minimized. Amongst them, optical losses as high as 30% light reflectivity are characteristic of bare Si substrates. In this chapter reduced reflectivity is reported by micro-texturing the front surface of a single crystalline silicon wafer using a diode pumped Nd:YVO₄ laser system with a computer controlled 3 axis galvanometer beam scanner. High laser scanning speeds (~1 m/s) and multiple passes resulted in microstructures that offer lower reflectivity than those achieved by current industrial texturing and SiNx:H coatings. The obtained micro-textures were further modified by a post-process cleaning method which gave a cleaner texture and reduced reflectivity. Moreover, texturing experiments were also carried out in an argon environment which was proved to improve the ablation efficiency of the process because the possibility of oxide formation during laser processing is eliminated in the presence of an inert gas. Additionally, in this chapter it was studied and demonstrated the impact of the
characteristics of laser-generated micro-structures (i.e. morphology, topography and periodicity) on the optical performance of Si surfaces exposed to solar irradiation.

5.1 Introduction

Silicon is the most widely used material for solar cells devices due to its semiconductor properties. As a well-established technology [73], silicon-based photovoltaic devices have been intensively researched over the past 30 years. The current challenge for the photovoltaic industry is to transfer research progress into an industrial environment by means of simple, economic and feasible processes. Optical, recombination and resistance losses, affect directly the efficiency of photovoltaic cells. Of primary importance are the optical losses because they account for the amount of energy that enters and leaves the cell. The aim of this research is to enhance the maximum energy that enters the cell and induce absorption in the most effective way once the photons are inside the cell at all available energy levels.

Antireflective coatings (ARCs) are commonly used to reduce optical losses, but they are optimized to absorb only at a limited wavelength range. A different method to reduce reflection is to texture the cell’s surface [74]. Texturing offers the advantage of not being wavelength-dependant plus a major enhancement on photon absorption [75]. This is due to the fact that texturing offers angled surfaces [76], making some light rays reflect between surfaces from one surface to another enlarging the photons’ optical path length and increasing their internal reflection [77]. This enlarged optical path, present only in textured surfaces [78], provides a change in the angle of incidence allowing the refracted photons to be absorbed closer to the p-n junction of the cell. This oblique coupling of light has been shown to produce an increase in the current generated.

Light trapping or internal reflection is the process in which photons are reflected back from the rear surface of the cell to the front, in which they encounter angled surfaces due to the texturing of the absorbing surface [79], increasing their probability of being absorbed. Efficient light trapping by multiple reflections can be obtained by pyramidal texturization achieving reflectivity measurements as low as
1.5% in combination with ARCs [80]. Zhao et al. [81] introduced a “honeycomb” surface texture in multicrystalline silicon which increases the optical thickness of the cell by a light trapping mechanism that causes total internal reflection of the absorbed light. They obtained efficiency results of 19.8% compared to the 18.6% for previous passivated emitter, rear locally diffused (PERL) cells. In this type of cells, developed at the University of New South Wales [82], typical texturing is pyramidal which has also been proved very efficient as a light trapping scheme with effective optical thickness enhancement factors as high as 40.

A variety of techniques could be used to texture a solar cell’s surface. Amongst them, dry etching has been shown to be successful at reducing reflectivity to 20% in the 600-900 nm range [83] by employing chlorine trifluoride (ClF$_3$). Winderbaum et al. [78] also applied RIE to micro-texture the surface of multicrystalline silicon solar cells, obtaining an attenuated average reflectivity of 5.6% and an increment in overall efficiency from 8.0% for un-textured cells to 9.89% for RIE-textured.

It has been demonstrated that laser texturing in solar cell applications is an efficient method for decreasing surface reflection and enhancing light trapping. The isotropic nature of the process makes it appropriate to be used in a variety of materials including polycrystalline silicon. This is a very important material because it represents half of the global photovoltaic production [76] and is considerably less costly than single-crystal silicon [84].

A laser texturization technique proposed by Abbott and Cotter [85] includes an ablation process followed by two different etching solutions. Etching is used in order to remove any slag from the ablated pits which can deteriorate electrical performance of the device. A Q-switched, Nd:YAG laser was employed to obtain a honeycomb pattern of conical pits. It was shown that the shape, aspect ratio and period of the structures, have a significant role in the optical characteristics of the substrate. Numbers of pulses affect the shape and depth of the ablated patterns with more pulses achieving higher aspect ratio structures. With deeper pits, surface reflection is greatly reduced. The depth range was between 10 and 50 µm, with 40
µm spacing. One of the purposes of the etching steps, besides removing slag, is to reduce the amount of laser-damaged material which can cause dislocations in the bulk of silicon and deteriorate its electrical characteristics. Recombination of minority carriers can occur due to the introduction of defects into the bulk material, sacrificing effective lifetime and open-circuit voltage. Although laser-induced defects might enhance Shockley-Read-Hall recombination, it has been demonstrated [86] that laser processing does not deteriorate cell electrical performance in a significant way.

Femtosecond laser irradiation in conjunction with ambient SF$_6$ and Cl$_2$ gases, was found to produce conical micro-spikes on silicon samples [87]. The micro-structured samples where irradiated with 500 laser pulses of 100 fs duration. The features were 40 µm tall with cross sections at the base of 60 µm$^2$ and 1 µm diameter at the tip. Further research findings into femtosecond micro-structuring of silicon have demonstrated almost 100% absorption for a broadband spectrum [88].

In addition to the already mentioned, several laser-texturing techniques [89-91] have been effectively developed yet need to be implemented in the photovoltaic industry. Modifications and improvements need to be done to these methods in order to increase their process speeds so they may suit a real industrial environment.

However, to the knowledge of the authors, there has not been a systematic study on the relationship between laser-processed c-Si surface’s morphology/topography/periodicity and its optical response to solar irradiance. So it is the intention of the present work to better understand this relationship and to achieve better reflectivity/absorption results by treating the samples in an argon environment. This work also analyses the effects of KOH etching to remove the defects and fine tune the geometry of the texture. In addition, the present results are compared with the standard texturization method of random-pyramid generation by KOH etching which is only suitable for single crystal Si samples.
Chapter 5-High Speed Laser Micro-texturing of Silicon for Improved Light Trapping

As this laser-texturization process is independent of crystal orientation it can be applied to multi-crystalline Si surfaces which are more widely used in the photovoltaic industry.

5.2 Laser Processing Experimental Procedure

A combination of laser texturing and chemical etching was used in this study. The obtained micro-structures were analyzed by means of optical microscopy (Polyvar MET microscope), scanning electron microscopy (Hitachi, S-3400N Type I), optical profiling (Wyko NT1100) and spectrophotometry (Analytik Jena, SPECORD 250). Their formation mechanism is investigated and their effect in surface reflectivity is discussed.

Pulsed laser irradiation of p-type single crystal Si <100>, boron doped, with a resistivity of 1-10 \( \Omega \cdot \text{cm} \), was carried out by means of a diode pumped Nd:YVO\(_4\) laser system (Laserval Violino, wavelength of \( \lambda = 532 \) nm, pulse duration of \( \tau = 8 \) ns, and a repetition rate of 30 kHz) with a computer controlled 3 axis galvanometer beam scanner.

The substrate surface was scanned by the laser beam having a spot size of 50 \( \mu \text{m} \) in diameter. Several trials at different scanning speeds and fluences were done in order to develop the structures that would give the lowest reflectivity. It was found experimentally that a 0.9 m/s scanning speed and fluence of 2 J/cm\(^2\), at a frequency of 30 kHz, resulted in uniform micro-sized pits that reduced the front reflectivity of the samples from 33\% to 23\% after only one scanning pass which shows the significance of texturing solar cells. As the number of passes was incremented, deeper microstructures were achieved and the reflectivity was observed to be noticeably further reduced, but this also implied an extended processing time and a larger amount of debris around the pits which is undesirable for photo-voltaic applications.
In order to remove the accumulated debris, an anisotropic etching solution of 30% KOH was used [92]. After laser processing, the samples were immersed in the solution for different time periods at a constant temperature of 60°C. The first effect observed was that the KOH unclogged and widened the pits. If the immersion time is prolonged, the structures will vanish from the surface and it will become flat again, which is detrimental for the process. However, it was determined experimentally that by etching the samples for 5 minutes in 30% KOH solution at 60°C, an improved texture is obtained, as will be later explained.

An additional set of experiments included the processing of the samples under the presence of an argon environment which resulted in deeper structures with a smoother surface finish. A KOH cleaning solution was also applied after such processing which demonstrated that the most important factor influencing the optical performance of the texturing is the depth of the laser-fabricated pits.

5.3 Results
5.3.1 Air environment – Morphology and Topography

When scanning at a lower fluence, the amount of energy that is delivered on a unit of area decreases, so the obtained structures exhibited a smaller diameter than that of the original beam spot. In the present case, the fluence was adjusted to 2 J/cm² and the scanning speed was set to 0.9 m/s, which implied the delivery of 1 pulse per spot. The sample was scanned following a linear regime with a hatch distance of 25 µm which resulted in a uniform square arrangement of oblated pits having ~ 31 µm and 28 µm along the principal axes (fig. 5.1(a-b)). The vertical profile of the structures indicated a pit depth of ~ 0.5 µm. Accumulated debris around the pits results in an elevation from a few hundred of nanometres to a few micrometers above the original surface (fig 5.1(c-d)). Periodicity can be controlled by adjusting the scanning speed, frequency and the hatch distance between line scans. In this case, as the periodicity between structures was set to 25 µm, the borders of the pits overlapped contributing to the increase of molten material around the edges.
Although some droplets of molten Si re-deposited in the bottom of the pits, this was virtually clean from debris and presented some waviness in the order of a hundred of nanometres.

When the same spot is targeted with several pulses by an increased number of scans, a deeper pit is formed and a significant amount of slag accumulates around. The deeper the pits, the lower the reflectivity because light rays have more chance to be reflected back between the pits’ walls and get absorbed. It was observed that as the structures get deeper, the excavated material builds up around the pit walls in an upward conical shape, see fig 5.2(a-d). From this combination of pits and conjoined walls in the form of cones, the light-trapping is greatly enhanced as will be seen in the next section.
Figure 5.2 SEM images of laser fabricated pits on Si after: (a) 10, (b) 20, (c) 30, and (d) 60 passes. The inset images show pit depth.

5.3.2 Air environment – Reflectivity Measurements

The total surface reflectivity curves were obtained for each of the micro-structured samples after multiple scanning passes by utilizing a spectrophotometer with a wall-mounted integrating sphere that covered the spectral range of $\lambda = 360$ to 1100 nm (see figure 5.3). A calculation of the solar weighted reflectance (SWR) was employed in order to consider the spectral distribution of solar energy in which photons with less energy than 1.1 eV (silicon band gap) are discarded due their inability to produce photocurrent, and photons above that value only contribute 1.1 eV of energy [93].
Figure 5.3 Comparison between the normalized photon flux of the solar spectrum (AM1.5) and the total reflectivity of different Si surfaces before and after laser micro-texturing.

This normalised photon flux (shown in figure 5.3) is needed to reveal how much of the solar spectra irradiance might be converted into electricity, and corresponds to the solar energy distribution reaching the earth after it has permeated through the atmosphere divided by the energy of an individual photon. Then the SWR can be expressed by [93]:

$$SWR(\lambda) = \frac{R(\lambda)S(\lambda)\lambda/hc_0}{\chi};$$  \hspace{1cm} (5.1)

Where \( R(\lambda) \) is the spectral reflectivity, \( S(\lambda) \) is the terrestrial solar energy distribution at conditions of Air Mass 1.5, \( h \) is Planck’s constant, \( c_0 \) is the speed of light in vacuum, and \( \chi \) is the normalising factor: \( S(\lambda)_{\text{max}}\lambda/hc \). This equation can be integrated over the 360-1100 nm spectra and solved by a finite element method in which \( n \) is the number of wavelengths for which data is known [94]:
The cross section of these structures (see figure 5.2 a-d) can help estimate the material removal rate for the set of optimised laser processing parameters obtained experimentally in the present work. This can be estimated to be 0.5 µm/scanning pass. However, due to the accumulation of material around the pit opening, the total microstructure depth (measured from pit bottom to cone tip) increases to 1 µm/pass which can be seen in fig. 5.4a. This relationship follows a linear fit that can be approximated by:

\[ y = 0.5 + 1.5x \]  \hspace{1cm} (5.3)

From figure 5.4b, it can be seen that a considerable reduction in reflectivity occurs when a number of 10 scanning passes is reached with almost a 50% suppression of reflectivity. As the number of passes is increased, the SWR % keeps decreasing in a rather exponential decay. It is seen that from 40 scanning passes the suppression of reflectivity falls at a rate of ~ 1% for every 10 passes. This tendency
dictates that if a sample is scanned by 60 passes, the texture will be composed of microstructures with depth of 60 µm and will reflect only 5% of the solar radiation (AM 1.5) at normal incidence.

5.3.3 Argon environment

In order to investigate the effects of structure formation in the absence of oxygen, the samples were laser-processed in an argon-filled chamber which suppresses the inherent oxide layer produced in an air environment. After one-single pass, no evident change was seen in the samples processed in the Ar-filled chamber, with pits exhibiting the same characteristics as of those processed in air. Nevertheless, as the number of passes was increased by 10, there was an evident change in the material removal rate. At this point the microstructure depth is increased from 10 µm (air) to 17 µm (Ar) (fig 5.5a). Above 20 scanning passes the material removal rate increases by 150% for all samples processed in Ar (fig 5.5 b-d).
Figure 5.5 SEM images of laser fabricated pits on Si in an Ar environment after: (a) 10, (b) 20, (c) 30, and (d) 60 passes.

The relationship between the microstructure depth and number of passes for this case is presented in fig. 5.6a and can be fitted to a non linear curve by the following equation:

\[ y = 1.41 + 1.46x + 0.005x^2 \]  

(5.4)

This enhanced ablation characteristic given by an Ar environment also extends its benefits to the SWR (%) reflectivity versus the number of passes (fig. 5.6b). As deeper structures offer a higher aspect ratio there is more opportunity for light to be reflected and get absorbed between the pit walls. This is more pronounced for samples scanned by more than 20 passes. The same decay in SWR (%) shown by samples processed in air is followed, but a larger decay constant accentuates the decline in reflectivity given by deeper microstructures.
5.3.4 KOH Post-Processing – Air

A considerable concern was the amount of material accumulation around the pits and defects generated in the material in laser surface texturing. A widely-used step to eliminate this unwanted and detrimental feature is to immerse the samples into a Potassium-Hydroxide solution. The etching rate of 30% KOH on <100> silicon is 0.4 µm/min at 60°C forming an anisotropic angle of 54.74° from the plane [95].

Two different etching effects on reflectivity could be identified: the first one was related to the clearing up of material around the pits and the anisotropic etch of the sidewalls and the second one corresponds to the decrease in structure height due to a prolonged exposition to the etchant. Therefore, etching time must be controlled so the benefits of structure height and angled walls can be used to attain the lowest reflectivity. This meant that for single-scan samples the etchant was in direct contact with the entire surface and the non-patterned surface is also affected. So for low aspect ratio micro-structures (~ 0.5 µm depth) the reduced-reflectivity effect was lost as the pits widen and disappear after only 1 minute exposure.

When samples that had been scanned 10 times were immersed in the KOH solution, texturing showed a more defined geometry, however flattening occurred.
and the etching effects deteriorate the optical performance of the texture. Based on experimental observations it was determined that etching of micro-structures is more suited for samples that possessed a structure height of at least 20 µm. This occurred because deeper structures obtained by multiple passes acquired an angled shape at the base which is inherent to the way in which KOH anisotropically etches single-crystal silicon in the <100> plane. Nevertheless, it was only after 20 scans, that the original height of 30 µm was able to resist the etchant effects. Sidewalls became more pronounced, and due to deeper structures, although flattening occurred the structures could still offer reduced reflectivity.

![Figure 5.7 SEM images of KOH-etched pits on Si after: (a) 20, (b) 30, (c) 40, and (d) 60 passes, processed in air.](image-url)
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In figure 5.7a, a square array of etched pits shows how their inner part resembles a V-shaped groove with an apex of 70.5°. The outer part is also characterised by angled walls but of a lesser angle from the plane which can be explained by a longer exposition of the outer parts of the pit with the etchant. In previous sections, it was shown how the structure depth plays a major role in the reduction of reflectivity. Moreover, in the present section it can be seen how the morphology revealed by the KOH etchant is significant for the optical performance of these structures. Even though 10 µm depth microstructures were reported to achieve a SWR of 18% without KOH post-processing (fig. 5.6b), the same depth for chemically etched microstructures gave a SWR of 26% (figure 5.8 a-b). This abrupt increase in reflectivity after KOH etching can be explained by a reduction in the steepness of the pits walls.

At 30 passes the morphology of the etched pits becomes more uniform in the sense that all the walls present the same angle of 54.74° with the plane and the bottom of each pit is not an apex but a square plane. As indicated in the graph of fig. 5.8a, etching removed ~ 10 µm from the top which resulted in an overall pit depth of 20.2 µm. From this point onwards, the reflectivity for etched samples was approximately 5% higher but remained stable for an increased number of passes.
From 40 passes and above, the etchant removed ~ 15 µm from the top and although all the samples were exposed to the same etching time, the way in which KOH attacked the material varied according to the areas of surface that were exposed for a longer time. For example, when the deepest structures obtained by 60 scanning passes were immersed in the KOH solution, the first effect was that the rim of the pits was cleared from any debris. Once this accumulated material is eliminated, the etchant starts reacting with the first layers of silicon and this can be seen in the top of the surface as small pyramids are formed around the more squared pits. At this point, the walls get smoother and the bottom starts showing the characteristic V-shape.

5.3.5 KOH Post-Processing – Argon

The samples that were processed in an Ar environment were also subjected to the KOH post-processing. The main advantage of this is that their enhanced ablation depth was still able to provide a low reflectivity over a wide spectrum (λ: 360 to 1100 nm) even after etching. The same pattern is followed: the debris around the rim was removed; top surfaces presented pyramidal etching, walls get a smoother finish, pit morphology changes from an oblated to a square profile and the bottom ends in a 70.5º apex.

![Figure 5.9](image-url)  
**Figure 5.9** SEM images of KOH-etched pits on Si after: (a) 60 passes (processed in Ar), and (b) Random KOH etching of s-c Si.
In figure 5.9a, a sample scanned by 60 passes and immersed in 30% KOH for 5 minutes is presented. The original depth was ~ 70 µm, and after etching decreased to ~ 50 µm. Figure 5.9b shows the typical pyramidal etching of an s-c Si surface that to the eye of the observer appears to be of matte gray in colour and not black.

Reflectivity measurements for both surfaces (fig. 5.10) showed that a pyramidal etching surface had a SWR of 10.5% whilst the laser texturing in Ar sample reflected only 3% over the solar weighted spectrum before KOH and 5 % after KOH. This confirmed that both, angled walls and microstructure depth are the factors that determine the amount of light that will enter the cell. As it can be seen from the pyramidal texture inset in fig. 5.9b, the pyramids height does not reach 11 µm and varies as etching is random. However their angled walls boost the probability of light to be absorbed. Thus, the optical performance of the deep laser-generated microstructures is above the current texturing industrial standard that can only be
applied to single-crystal wafers as it does not only offer angled walls but deeper structures.

In standard Si-based photovoltaic applications, in order to make the pyramidal etching more efficient, an extra layer of anti-reflective coating has to be added which suppresses light completely for some wavelengths but not for the whole spectrum. On the contrary, the laser micro-texturing introduced in this work suppresses the reflectivity in a virtually constant trend for the whole 400-1000 nm wavelength range.

5.4 Discussion

Diode-pumped solid state (DPSS) lasers are a widely used tool to micro-machine Si substrates [96]. Of special interest are the ones which operate in the nanosecond regime. Despite their low pulse energy, this type of laser can achieve ablation thresholds through small spot sizes and high pulse-repetition frequencies [97].

The nano-second laser textured surfaces presented in this chapter resulted in a very effective way of suppressing light reflection from the front surface. It was shown that as the number of scanning passes is increased, the laser beam etches the material producing deeper structures. This was accompanied by a cumulative amount of debris and defects around such features. The formation mechanism of a single pit can be explained as follows: when laser irradiation meets the Si surface, electron excitation occurs due to photon absorption. This absorbed energy is then transformed into heat by means of a process known as “electron-phonon” relaxation which transfers the energy to the material by lattice vibrations. This results in an increased temperature and subsequent melting.

In the present case a thermally-driven, melt-expulsion by laser generated vapour recoil pressures mechanism is identified as responsible for the generation of the smooth-shaped craters with a rim around them. At intensities below $1.1 \times 10^9$
W/cm², the rim’s volume of mass is approximately equal to the crater’s volume of mass which confirms that molten material is expelled and re-solidified at the edges of the crater [98, 99]. For the craters exhibited in section 5.3.1, the laser intensity was \( \sim 2.5 \times 10^8 \) W/cm² which places the ablation in the above mentioned regime. From volumetric calculations, the ratio of the rim volume to the crater volume for the crater shown in figure 5.1(a) is also \( \sim 1 \), which was the same crater morphology exhibited by the samples processed in an argon environment. This material re-distribution outside the crater is also seen in the multiple-passes process; however the ablation efficiency is improved by a factor of 1.5 when the texturing is carried out in Ar environment.

The introduction of a different background presents a very useful way to suppress the presence of an oxide layer formed in air after the first irradiated pulses [100, 101]. Laser-induced oxidation is known to be detrimental for the ablation rate as coupling of light into the crater might be affected by a ‘light trapping’ thin oxide layer [42].

The use of chemical-etching cleaning assisted in unclogging the pits and clearing the surface from laser-damaged material. A solution of 30% KOH was selected because of its anisotropic etching nature which suited the single-crystal material (Si <100>) used in the experiments. The effect of this cleaning measure was not perceived for relatively shallow pits (<20 scans), but for deeper pits it was key in defining the geometry of the structures. The bottom of the pits appeared more delimited, and their sidewalls were sharpened forming an angle with the surface. It happened that this combination of pits and pyramids offers a reduced solar weighted reflectivity which might reach 5% for the 360-1100 nm spectrum, if correct processing parameters are applied.

Etching time must be carefully controlled so no further flattening of the structures occurs. It has to be remembered that good light-trapping texturing depends in how many times light is reflected in the interior walls of the structures to get some absorption into the material on each reflection. Thus, depth and geometry of the structures are critical aspects for such absorption mechanism.
Contrary to wet-etching texturing in which pyramids are formed randomly, this investigation has shown that the spacing between structures can be readily controlled by the scanning speed, frequency and hatch distance. As it was identified by reflectivity measurements, these parameters play an important role on the optical performance of the texture. For example, for the same number of passes, very spaced or close structures may result in a different effect on reflectivity.

![Figure 5.11](image)

**Figure 5.11** SEM images of laser fabricated pits on Si in an air environment after 40 passes: (a) scanning speed of 1.8 m/s, hatch pitch of 50 µm (b) scanning speed of 0.9 m/s, hatch pitch of 15 µm (inset: initial texture after 1 pass).

This can be appreciated in figure 5.11(a). Such a texture was obtained after 40 laser passes but the scanning speed was modified to 1.8 m/s and the hatch pitch to 50 µm. This resulted in a twofold increase in the spacing between the structures compared to the texture presented in section 5.3. As the speed was increased, the number of pulses per pass deposited in the surfaces changes from ~2 to ~1 which also has an effect in the pit’s depth (as it is shown in the inset). Droplet deposition around the edges is also more pronounced and also the pit appears to acquire a larger size as there is not overlapping and the accumulated material in the rim is not constricted upwards by the nearest crater. This also affects the height of the rim which was seen to diminish.
In figure 5.11(b), the spacing is altered by a reduction in hatch distance down to 15 µm. This creates a closed overlap between structures and less coupling of light into the bottom of the pit by each pass which results in poorer ablation efficiency. Even though 40 passes were delivered to the substrate, the texture’s quality is affected from the first pass (shown in the inset figure). As the structures are too close from the initial scanning pass, light cannot be confined to a specific spot, but gets scattered by a denser population of peaks and valleys.

Figure 5.12 Total reflectivity of laser-treated surfaces in air environment: (a) different speed and hatching distances; (b) Tight spacing after single and multiple passes.

Reflectivity graphs give an insight of how periodicity and morphology changes do have an impact in the texture's optical performance. Figure 5.12(a) portrays the reflectivity curves for a bare surface and samples scanned with 40 passes but with different spacing arrangements. Even though reflectivity is reduced for all 3 laser-treated surfaces, the minimum value is achieved by a square arrangement in which the periodicity Λ is very close to the pit dimension. Very spaced craters show a higher reflectivity possible due to the reduced structure height and less angled surfaces for the light to be reflected and get trapped. Tightly spaced structures fail to provide an opportunity for the laser beam to be confined into the bottom of the pits which results in less structure height, hence a reduction in total reflectivity.
In fact, a rougher surface like the one obtained by a reduced hatch distance, provides almost 50% reduction in reflectivity after just 1 pass. But this condition deteriorates with increased passes, as it can be seen in figure 5.12(b), where after 40 passes the reflectivity curve is shifted up. It is believed that more laser light is absorbed after the first pass, but with subsequent scans the laser is not delivered into localised ablation sites but rather absorbed by an unstructured roughness and translated into more heat and melt. The scan pacing that could be varied in this study was an advantageous condition.

Another factor that was noticed to have an effect on the final shape of the structures was the laser fluence selected to fabricate the structures. If too much pulse energy is deposited in the same area, the ablation spot becomes larger as well as the amount of melted material that re-solidifies around the edges. This can have an unfavourable effect on the optical performance of the texturing as the morphology of the pits changes due to more molten material lying on top of adjacent structures. Also, if the pulse energy is too low, less material will be removed, influencing the pits’ aspect ratio and their light trapping role.

Based on an optical enhancement factor proposed by Mutitu et al [102], the light trapping function of the micro-structures can be compared to a solar cell without any antireflection coatings and/or texturing. This measurement represents the ratio of the absorbed light by a solar cell with light-trapping structures to the absorption of a bare silicon solar cell [102]:

$$EF(\lambda) = \frac{\int_{\lambda=360}^{\lambda=1100} A_L(\lambda')S(\lambda')d\lambda'}{\int_{\lambda=360}^{\lambda=1100} A_B(\lambda')S(\lambda')d\lambda'}$$  \hspace{1cm} (5.5)

In equation 5.5, $A_L(\lambda)$ refers to the absorption spectrum of a light-trapping solar cell; $A_B(\lambda)$ accounts for the absorption of a bare silicon solar cell, $S(\lambda)$ corresponds to the solar energy distribution (AM1.5) for the spectrum that covers $\lambda$: 360 to 1100 nm wavelengths. The amount of absorbed light can also give an
indication of the short circuit current generated by a solar cell; this is expressed by the following equation [103]:

$$J_{sc} = \frac{q}{hc} \int \lambda^0 A(\lambda')S(\lambda')d\lambda';$$  \hspace{1cm} (5.6)

Where $J_{sc}$ represents the short circuit current density, $q$ is the electron charge; $h$ is the Planck constant, and $c$ is the speed of light. If the internal quantum efficiency is considered to be 1, and the internal carrier collection efficiency is discarded, the only losses associated to the efficiency of the cell are the optical losses. It is the intention of the present investigation to demonstrate a laser-based approach for minimising such losses.

**Table 5.1** Enhancement factor and short circuit current density for different solar cell surface types.

<table>
<thead>
<tr>
<th>Surface type</th>
<th>Enhancement Factor (EF(λ), 360-1100 nm)</th>
<th>$J_{SC}$ (mA/cm²) (360-1100 nm)</th>
<th>$J_{SC}$ enhancement (360-1100 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Si</td>
<td>1</td>
<td>25.9</td>
<td>-</td>
</tr>
<tr>
<td>Texture after 1 scanning pass</td>
<td>1.12</td>
<td>28.85</td>
<td>11.4%</td>
</tr>
<tr>
<td>Texture after 60 passes in air</td>
<td>1.42</td>
<td>36.6</td>
<td>41.3%</td>
</tr>
</tbody>
</table>

Table 5.1 gives an illustration of the optical performance of the laser micro-structures obtained in this work. As demonstrated in the results section, deeper features will couple more light into the material which can be directly translated into a short-circuit current boost of up to 41.3%. Actually, the calculated maximum $J_{SC}$ for a 390 µm-thick cell is 38.8 mA/cm², which means 100% absorption in the 360-1100 spectrum.
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Figure 5.13 (a) Absorption and (b) transmission spectra for bare Si and laser micro-textured surfaces. Transmission measurements were carried out using a spectrophotometer with a wall-mounted integrating sphere.

Laser structuring can offer a very close value to one of 100% absorption, even without an antireflection coating and a back-reflector. This can be better visualised in figure 5.13a in which absorption curves for the 360-1100 nm spectrum are presented. Although silicon is a weak absorber in the near-infrared band edge (800-1100 nm), it is seen in figure 5.13b how the oblique coupling of light by laser micro-texturing greatly reduces the probability of light escaping through the back of the cell for this range.

Figure 5.14 (a) Simulated short-circuit current density for a single-crystalline solar cell with no AR coating/texturing, for a laser micro-textured solar cell and the maximum limit for total absorption of light; (b) simulated short-circuit current for the near-infrared spectrum.
Figure 5.14(a-b) shows the modelled short circuit current as a result of the proposed optical improvement. It can be seen that a laser micro-textured solar cell surface offers an optimum electrical performance close to the theoretical maximum limit in which all light is absorbed by the cell in the 360-1100 spectrum. In practice, other losses associated with surface recombination and resistance directly affect the performance of the cell, but these are outside the scope of the present work. An important aspect of the laser-textured surface is that even without the inclusion of a back-reflector (which is a common practice in the photovoltaics industry) the amount of current generated in the near-infrared is very close to the maximum limit. This can be explained by a reduction in both reflectivity and transmission due to an enlarged optical path given by deeper structures with angled walls.

5.5 Conclusion

This chapter has studied the response of light to micro-structures fabricated on single-crystal Si by employing a diode pumped Nd:YVO₄ laser system (λ: 532 nm, τ: 8 ns). Some unique structures have been produced after laser processing (both in air and argon gas) and KOH etching. By following a linear scanning regime, pits with constant spacing were obtained. As the number of passes were increased, such pits became deeper and after etching, their walls acquired a steep and angled orientation which enhanced the light trapping mechanism provided by the texture. It was found that it was possible to achieve SWR below 5%, following an optimum operating window for laser structuring by multiple scanning passes (60) at a scanning speed of 0.9 m/s and fluence of 2 J/cm², at a frequency of 30 kHz.

It was found that processing in argon offered better ablation efficiency with an enhancement factor of 1.5, which resulted in deeper structures fabricated by the same number of passes than in air. This is of importance because, as shown in this study, reflectivity is strongly related to the depth and morphology of the texture. Also, processing in argon proved to be beneficial as a concern is the reduction of the laser-processing time per wafer, as a larger number of passes makes the process slow.
even if the scanning speed is reasonably fast. Further investigation in this area should be carried out by employing a tighter focus spot and consequently larger fluence values.

A more profound understanding of such light trapping mechanism was provided by theoretical modelling of the optical performance of these micro-structures. Devoid of antireflection coatings and a back reflector, the laser micro-textured surfaces proved to perform suitably well in the short-circuit simulation; even in the 800-1100 near infrared spectrum for which silicon is known to be a weak absorber. As a final remark, this technique is intended to be tested in real photovoltaic devices to assess its practicality and future commercial implementation.
By rapidly scanning a 532 nm diode pumped Nd:YVO₄ laser beam at nano-second pulses below the ablation threshold, a uniform array of nano-bumps of less than 2 nm in height (diameter of around 20 µm) was generated on a p-type <100> Si wafer. This height is two orders of magnitude lower than previously reported values. The array was produced at 30,000 bumps per second. The effect of laser fluence (energy density) and scanning speed on the characteristics of the nano-bumps is investigated and the wettability of the laser nano-textured surfaces is examined. The mechanisms of nano-bump formation are discussed. Also presented are the application of the technique for debris free, invisible marking/texturing of silicon and the recognition of such marks/patterns.

6.1 Introduction - Laser marking on Silicon

Laser marking of crystalline silicon is a well established process with more than 40 years of applications in the semiconductor industry. Marking of electronic components, wafers, integrated circuits and other items made of this widely used material is of importance to the manufacturers because it allows for information identification, serialization, traceability, copyrighting, and even for decoration [85].

Laser marking of silicon started with “Hard Marking” technology which consisted of laser marks of 5-20 µm depth, fairly visible and durable but with a
significant amount of debris around them. Such marks became incompatible with the manufacturing process as the demand for smaller devices increased. This required a new technology by which splatter, debris and depth could be diminished to a minimum. “Soft Marking” by diode pumped solid state (DPSS) lasers was then introduced (height to width aspect ratio of marks \( \sim 0.01 \)), followed by “Super Soft Marking” (depth of marks \( \sim 2.6 \, \mu \text{m} \)) in which debris generation was entirely eliminated [104]. However, the drive to achieve smaller feature sizes, larger output and reduced costs has pushed the development of new marking techniques towards the nano-scale.

Micro-peak formation on crystalline silicon [105] has been reported as a feasible, novel marking technology. By directing a Nd:YAG laser beam to a programmable LCD mask, a square array pattern is projected onto a silicon surface. Micro peaks obtained after the laser irradiation exhibit a size of 3.6 \( \times \) 3.6 \( \mu \text{m}^2 \), a period of 4.5 \( \mu \text{m} \) and a height of 0.3 \( \mu \text{m} \). They are claimed to be easily readable under simple lighting due to their depth to width aspect ratio which can be set to 0.15 under the correct laser parameters. The aspect ratio in conventional laser marking is a very important feature because it determines the visibility of each mark given by the contrast between bright and dark parts when subjected to some sort of lighting.

Even smaller laser-fabricated features such as smooth craters on \(<100>\) silicon (depth of 35 nm and diameter of 10 \( \mu \text{m} \)) have already been demonstrated [106]. Such structures were claimed to be oxide-free after being processed by 8 ns pulses from a Nd:YAG laser (\( \lambda = 532 \, \text{nm} \)) with a fluence of 3 J/cm\(^2\). Such surface modification was attributed to thermal melting and a thermo/chemo-capillary flow. Similar topography changes in the nanometre scale have been obtained in Polyimide [107]. Depending on the laser fluence applied, three regimes were identified: holes (depth of 163 nm), humps (height of 17 nm) having a small dip at the top (depth of 7 nm), and bumps (height of 21 nm). Formation mechanisms of the last two topographies were attributed to amorphization of the material, thermal or non-thermal fragmentation of the polymer chains and plastic deformations due to residual stresses introduced at elevated temperatures.
In this chapter, uniform arrays of nano-bumps of less than 2 nm height (diameter of around 20 µm) are demonstrated on a silicon wafer surface. This height value is two orders of magnitude lower than the above reported values for laser marking applications. The effect of laser fluence and scanning speed on the characteristics of the nano-bumps is reported along with the wettability of the laser nano-textured surfaces. The nano-bumps formation mechanism (aspect ratio of $5 \times 10^{-5}$ and height of 1-2 nm) is investigated.

6.2 Laser Processing Experimental Procedure

Pulsed laser irradiation of p-type, single-crystal Si <100> (boron doped and resistivity of 1-10 Ω·cm) was carried out by means of a diode pumped Nd:YVO$_4$ laser system (Laservall Violino, wavelength of $\lambda = 532$ nm, pulse duration of $\tau = 8$ ns, and a repetition rate of 30 kHz) with a computer controlled 3 axis galvanometer beam scanner. The substrate surface was scanned by a Gaussian laser beam having an elliptical shape due to astigmatic aberration of the focusing lens. Measurement of the ablation sites using optical microscopy led to the following spot dimensions: 50 µm along the minor axis and 80 µm along the major axis. Fluence values in this chapter are based on such measurements.

When controlling the intensity of the Gaussian beam, a low fluence of 0.72 J/cm$^2$ resulted in uniform structures of only 1 nm in height and ~ 20 µm in width. Processing parameters such as power and scanning speed were varied in order to obtain marks that could not be easily detected unless they were exposed to a difference in temperature with water/moisture condensation. It was found that laser processing at a fluence of 0.72 J/cm$^2$, repetition rate of 30 kHz and a scanning speed of 1 m/s, resulted in very shallow marks only perceptible to the eye after some minutes of being stored in a cold box at 0°C or when the surface at 21°C is exposed to warm vapour (e.g. at 36-37 °C). A single pulse per spot was necessary to achieve a nano-bump structure formation.
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Considering the aforementioned laser parameters, an area corresponding to 1 cm$^2$ was processed by following a linear scanning regime to cover the whole surface with nano-bumps. Hatch distance between scanning lines was adjusted to 25 µm. In this way, a regular square array of the structures was formed. Total processing time for this region was about 4 seconds. Moreover, arbitrary shapes (such as letters and spirals) made of these nano-bumps were created and seen without the need of any special lighting or lenses.

6.3 Results

6.3.1. Topographical and morphological characteristics

Topography and morphology of the nano-bumps were examined with the aid of a high resolution (0.1 nm in the z-axis) white light interferometer (Wyko NT1100) and a scanning electron microscope (Hitachi S-3400N). Initially, a bare and clean silicon sample was analyzed (fig. 6.1(a)). Then, different laser fluences were used to determine the threshold for topography modification at a fixed repetition rate of 30 kHz and a scanning speed of 1 m/s.

The first signs of structuring (i.e. 1 nm high bumps emerging from the laser treated area) appeared when the fluence was 0.54 J/cm$^2$. However, the obtained structures were not organized in a uniform array. When the laser fluence increased to 0.72 J/cm$^2$, a regular array of well defined bumps was obtained as shown in figure 6.1(b). From the height profiles in figure 6.2(a) and (b), it was determined that such bumps have a diameter of ~ 20 µm, a height of ~ 1 nm and period of ~ 25 µm.
Figure 6.1 White light interferometer (Wyko NT1100) images of silicon sample surface (a) before laser processing and (b) after laser processing (nano-bumps on top) at a fluence value of 0.72 J/cm².

Figure 6.2 Typical height profiles (Wyko NT1100) of nano-bumps fabricated at laser fluence of 0.72 J/cm², showing (a) a radius of ~10.2 µm and height of ~1 nm; (b) nano-bumps period of Λ = 23 µm.

An increment in the fluence to 0.83 J/cm² generated a random mixture of bumps and craters in the same laser treated area, as seen in figure 6.3 (a). For bumps, the diameter, height and periodicity remained almost the same as in figure 6.2. The craters were around 3.5 nm in depth and ~25 µm in diameter (including a small rim around them). With a subsequent increase in fluence to 0.94 J/cm², bumps completely vanished from the surface and were replaced solely by craters (figure 6.3b). The height profile of such craters is shown in figure 6.4(a) and (b).
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Figure 6.3 White light interferometer (Wyko NT1100) images of (a) a combination of craters and bumps on silicon sample surface after laser processing at a fluence of 0.83 J/cm$^2$; (b) craters formed at a laser fluence of 0.94 J/cm$^2$.

Figure 6.4 Typical depth profiles of craters generated on silicon surface at a laser fluence of 0.94 J/cm$^2$, showing (a) radius of $\sim$ 10.2 $\mu$m and diameter of $\sim$ 3.7 nm; (b) craters period of $\Lambda = 29$ $\mu$m.

Figure 6.5 summarizes the dependence of the nano-structure height (negative values indicate structure depth) as a function of laser fluence. A noticeable change in depth (i.e. a few hundred nanometers) and a larger amount of debris around the craters was observed when the laser fluence was set above 1.5 J/cm$^2$ (this is not shown in figure 6.5a).
Besides laser fluence, the scanning speed is another important system parameter affecting the process. It should be noted that the repetition rate was fixed to 30 kHz and the scanning speed to 1 m/s; this corresponds to one pulse per spot. As the scanning speed changes, the number of pulses per spot will change and the final sample surface topography and period of the structures will vary accordingly.

Figures 6.6 and 6.7 summarize the dependence of structure height and structure period as a function of scanning speed within a range from 0.8 m/s to 3.0 m/s, at a fixed laser fluence of 0.72 J/cm² and a fixed repetition rate of 30 kHz. Within this scanning speed range, structuring resulted in a uniform array of nano-bumps with a clearly defined height and period. At a scanning speed of 0.6 m/s (3 pulses per spot) the obtained structures became irregular and craters and nano-bumps were mixed and overlapped without clear spacing between individual spots. When
the scanning speed was decreased to 0.1 m/s (16 pulses per spot) a dotted line of ~12.05 µm in width and 10 nm in depth was generated. As the scanning speed decreased further, line width and depth kept increasing.

![Figure 6.6 Nano-bumps height as a function of scanning speed.](image1)

![Figure 6.7 Nano-bumps period as a function of scanning speed.](image2)

The scanning speed effect was further studied for other laser fluences. Figure 6.8 shows the dependence of structure (nano-bumps) height as a function of scanning speed at laser fluences of 0.54 J/cm² and 0.63 J/cm². It was noticed that for fluence values below 0.72 J/cm² and scanning speeds of 0.2 to 3.2 m/s, the surface was either
unaffect ed (structure height of 0 nm) or populated by nano-bumps (structure height < 1 nm).

![Figure 6.8 Variations of nano-bumps height versus scanning speed for laser fluences of 0.54 J/cm$^2$ and 0.63 J/cm$^2$.](image)

Figure 6.8 Variations of nano-bumps height versus scanning speed for laser fluences of 0.54 J/cm$^2$ and 0.63 J/cm$^2$.

On the other hand, as shown in figure 6.9, when the fluence was 0.72 J/cm$^2$ and the scanning speed was less than 0.4 m/s, craters with depths of a few nanometres (negative-value in height) covered the laser treated surface. The craters only changed to nano-bumps (height of around 1 nanometre) when the scanning speed increased to 0.8 m/s. However, the crater-to-bump transition trend was not noticed for slightly higher fluences of 0.83 and 0.94 J/cm$^2$, for which craters do not develop into 1-nm-height nano-bumps even if the scanning speed is increased. This observation will be further discussed in section 6.4.2.
6.3.2 Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis

Different computer designed patterns can be easily transferred to a silicon surface through an integrated galvanometer scanning system. Figure 6.10 shows SEM images of (a) a spiral pattern and (b) cross grids fabricated on a silicon surface using the following parameters: laser fluence of 0.72 J/cm$^2$, scanning speed of 1 m/s and laser repetition rate of 30 kHz. These laser marks are made of nano-bumps. Clearly a strong contrast can be seen in the SEM image for the processed and non-processed regions. The irradiated areas exhibit the white halo which is typical for an amorphous film [108]. This suggests that the material could have gone through a phase transition from single-crystal to amorphous.
Figure 6.10 SEM images of laser marks on a crystalline silicon surface made of laser generated nano-bumps at laser fluence of 0.72 J/cm$^2$, scanning speed of 1 m/s and repetition rate of 30 kHz: (a) spiral pattern, (b) cross grids.

SEM images of the craters were also analyzed to detect the presence of a possible amorphous layer when the fluence is above the ablation threshold. In figure 6.11 a white region around the craters is observed, it follows the elliptical shape of the Gaussian beam, exhibits a ‘ring’ feature, and is similar to the reported laser amorphized morphologies in the literature [109, 110].

At a laser fluence of 1.14 J/cm$^2$, the craters are only a few nano-metres deep, and the rim around them is ~ 0.5 nm high. Because of the Gaussian distribution of the beam, the fluence at the centre is sufficiently high to ablate the material. However, the surrounding white annulus could be explained by a phase transition due to lower laser energy delivered to this area. When the laser intensity is decreased, the modified areas are smaller than the nominal laser spot. In the reported case this results in half the original size along the minor axis of the beam and hence the reduction in the structure diameter.
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Figure 6.11 (a-b) SEM images of a laser processed silicon sample at a laser fluence of 1.14 J/cm², scanning speed of 2.0 m/s, frequency of 35 kHz and a hatch distance of 0.07 mm.

In order to further investigate the chemical composition of the laser generated patterns, energy-dispersive X-ray spectroscopy (EDX) analysis was performed. According to the EDX results (shown in figure 6.12) no trace of oxygen was found in the samples which may exclude oxidation from the process. The white regions in figure 6.10 and 6.11 are thus purely silicon in non single-crystalline states (either amorphous or poly-crystalline).

Figure 6.12 EDX spectrum of a laser generated nano-crater (shown in figure 11b). The SUM SPECTRUM is a software tool that calculates the total intensity counts of all the pixels in the image per energy channel.
6.3.3 Surface post-processing: Potassium Hydroxide (KOH) etch

To further determine the possible phase-change of the laser processed patterns, a chemical etching method was used. It has been reported that an amorphous layer on silicon can be used as an etch mask against KOH for micro/nano fabrication purposes [109, 111, 112]. Based on this, a sample exhibiting an array of 1 nm bumps (figure 6.13a) was immersed in a 30% wt. KOH solution at 55°C for 90 seconds and under constant stirring. Immediately after this, it was rinsed with abundant deionised water to stop further etching.

The results of this post-processing step are shown in figure 6.13b. The laser-generated nano-bumps were not etched, while the non-treated regions were affected by the etchant. Thus, the laser processed areas masked the material against the typical effects of KOH in silicon which is readily etched in the <100> plane [113].

![Figure 6.13](image)

**Figure 6.13** Wyko images of a laser-treated silicon sample exhibiting a uniform nano-bumps array, generated at (a) a laser fluence of 0.63 J/cm², 30 kHz, 1 m/s, and hatch distance of 0.05 mm; (b) same surface after being immersed in a KOH solution at 55°C for 90 seconds.

The corresponding height profiles are presented in figure 6.14. It can be seen that after KOH etching, the nano-bumps base descends to ~ 28 nm. This means that the etch ratio of processed region was almost 30 times lower than that of the nano-processed crystalline regions. This etch ratio value agrees with the result from Kawasegi et al. when they etched an amorphous Si layer formed by magnetron
spattering [111]. Although Lam et al. [114] have suggested that at low fluences single-crystal Si could undergo a phase change to poly-crystalline, which could be excluded in this case due to the fact that the etching rates were similar for crystalline and poly-crystalline silicon when they were exposed to 30% wt. KOH [115].

For the laser-generated nano-bumps obtained with a laser fluence of 0.54 J/cm² (figure 6.15a) which displayed a lower height around 0.8 nm (figure 6.16a), a longer etching time (120 seconds) was used. As can be seen in figure 6.15b, the laser generated nano-bumps remained on the surface and the surrounding non-processed areas were etched much quicker resulting in a bump height of around 27 nm (figure 6.16b). In this case it was possible to distinguish the elliptical shape of the Gaussian beam which was made visible thanks to a longer exposure to the wet etchant. When the etching time was further extended, the nano-bumps started to diminish in height and eventually disappeared from the surface. This indicates that the laser-modified material was entirely removed and could no longer be used as an etch-stop mask.
Figure 6.15 Wyko images of a laser-treated silicon sample exhibiting a uniform nano-bumps array, generated at (a) a laser fluence of 0.54 J/cm$^2$, repetition rate of 30 kHz, scanning speed of 1 m/s, and hatch distance of 0.04 mm; (b) same surface after being immersed in a KOH solution at 55°C for 120 seconds.

Figure 6.16 Height profile of nano-bumps array at (a) a fluence of 0.54 J/cm$^2$ and scanning speed of 1 m/s (height is ~ 0.8 nm); (b) same surface after being immersed in a KOH solution at 55°C for 120 seconds (height is ~ 26 nm).

6.3.4. Wettability Characteristics

The presented nano-structures on Si changed the surface wettability of the material. In this study it was observed that vapour condenses into water drops of different size depending on the processed and non-processed areas. This vapour condensation effect helps the observer to easily recognize the ‘optically invisible’ nano-bumps which otherwise can only be detected by a white light interferometer or atomic force microscope. Figure 6.17 shows several examples of such characteristic wetting behaviour. The spiral rings and letters ‘LPRC’ were scribed over the silicon surface. The contour of the letters was patterned with the 1 nm high bumps as
previously described. Following their immersion in warm vapour, drops of clearly larger size (13-23 µm) covered the nano-bumps while smaller drops (5-7 µm) dwelled in the unmarked areas. Such difference in drop size is responsible for the change in visibility of the markings. Clearly, the laser marked areas are more hydrophilic thus exhibiting a larger contact line for the liquid and solid interface (lower liquid/solid contact angle). The observed change in the wetting characteristics of laser marked surfaces depends also on the ambient and substrate temperatures because this permits condensation to occur. A larger difference between both temperatures will give a more perceptible ‘invisible marking’ effect.

Figure 6.17 Recognition of laser marks after being exposed to warm vapour. The difference in water drops at the micro scale allows the viewer to see by means of an optical microscope: (a) a spiral ring, (b) ‘LPRC’ letters.

6.4 Discussion

6.4.1 Wetting behaviour before and after laser processing

Crystalline silicon will inherently grow a native oxide layer (1-2 nm high) after polishing, which makes the material more susceptible to surface contamination [116]. Since surface wettability is mainly influenced by the nature and arrangement of the top surface atomic layers [117], a measured contact angle of θ = 58° in the non-treated samples is the result of the interaction of water molecules with Si-O
bonds on the top surface. This is consistent with the reported values of Dixit et al. [118].

Considering that the laser processing was done at air conditions, the observed reduction in contact angle at the micro-scale in the treated samples might have occurred due to the introduction of more Si-OH bonds (silanol groups). This could be explained by a strong interaction of the water molecules in the ambient environment with the dangling bonds from the laser-modified amorphous material.

These silanol groups will make the surface layer more complex because they can permute to form a larger number of different chemical species which will exhibit distinct hydrophilic properties [119]. The chemical behaviour of more silanols created in the surface of the material during the nano-structure generation and possible phase-change transition, may clarify the noticeable difference in wettability seen on the marks at the micro-scale.

Laser surface treatment has been used by other authors to modify the wettability and adhesion characteristics of silicon [120]. By employing the 4th harmonic of a Nd:YAG pulsed laser (\(\lambda = 266\) nm) to irradiate a silicon sample, they noticed a decrease in contact angle and a change in the surface chemical composition of the material. A laser power of 0.8 to 0.9 W, and a scanning speed of 100 \(\mu m/s\) led to a decrease in contact angle from \(\theta = 47^\circ\) (before laser processing) down to \(\theta = 0^\circ \sim 22^\circ\) (after laser processing). Energy dispersive X-ray analysis enabled the authors to determine the relative content of oxygen after laser treatment and X-ray photoelectron spectroscopy confirmed the presence of (-OH-) bonds in large proportions compared to other chemical species. Thus, it was suggested that such an oxygen-enriched surface enhanced the hydrophilic behaviour of the samples and hence the improvement of the adhesion forces on the surface. It was also observed that after laser treatment the contact angles were inversely proportional to the surface roughness, which also played a role in increasing the adhesion forces. It has to be remembered that such reported contact angle values for the laser treated and untreated surfaces were measured at the macro-scale by the sessile drop method. These values may vary from the actual contact angles of water drops condensing at
the micro-scale on a Si surface, as seen in the wetted laser-marks reported in this section (figure 6.17).

In the present study, the effect of surface roughness on the contact angle measurements is deemed as negligible. This is because in the samples the magnitude of the roughness is too small (< 40 Å) to affect the wetting behaviour of the laser treated surfaces. This is in contrast to many of the micro and nano-structured surfaces studied by other authors [121-127] wherein the roughness is large enough to affect the surface contact angles. An example of how the wettability of a surface can be modified by laser micro and nano-structuring was demonstrated by Zorba et al. [128]. They successfully created a wettability gradient in a crystalline Si surface using a femto-second laser. When the authors varied the fluence, different microstructure morphologies (e.g. micro-ripples and micro-spikes) altered the wetting properties of the material and made it more hydrophobic. At laser fluences above 1 J/cm², they observed that nano-metre features covered the micro-features, increasing the overall roughness but contributing in a lesser way to the hydrophobic behaviour of the samples. Although a disordered Si layer (a few nanometres thick) was identified in their laser-processed samples, micro-structuring was considered to be the main mechanism behind the high contact angles obtained.

In this current investigation it is suggested that anisotropic wetting has been made possible due to a modification in the arrangement of atoms in the first layers of the material, apparently when it changes from crystalline to amorphous. It has also been considered that the aspect ratio of the nano-bumps is too low (5x10⁻⁵) in order to alter the wetting properties at the surface. Besides helping identify the low-aspect marks, this wetting behaviour could be employed in the preparation of very low-aspect ratio micro-fluidic channels. An example of this is shown in figure 6.18 wherein it can be appreciated how long water drops tend to elongate and spread along the laser-patterned areas.
Figure 6.18 Elongated water drops on the location of the laser marks show how these could be used as low-aspect ratio micro-fluidic channels.

### 6.4.2 Surface modification

The laser fluences used in this study had very unique effects on the material (i.e. laser-induced amorphization). Acknowledged as interactions below the ablation threshold [129], such effects are noticeable in different ways: surface morphology and microstructure, presence of defects, and depletion of components. In the present case, surface morphology (i.e. first signs of nano-bump formation) became an outcome when the amorphization threshold was visibly identified at a laser fluence of 0.5 J/cm². With increased fluence, at 0.72 J/cm² the nano-bumps are at their highest (~ 1.2 nm) and it is not until 0.83 J/cm² that the ablation threshold takes place characterized by a decline in nano-bump height (< 0.9 nm) and the generation of craters accompanied by an outer rim (see figures 6.1 and 6.3).

The laser-induced phase transition from the single-crystalline to the amorphous state in Si by a nanosecond laser was first reported by Tsu et al. [108]. They produced a thin amorphous layer by employing the fourth harmonic of an Nd:YAG laser ($\lambda = 266$ nm, $\tau = 10$ ns). By electron diffraction patterns they noticed that such layer was characterized by a white colour and had a slight thickness variation above the original surface. The authors concluded that such a phase change occurs when melted Si is rapidly cooled down without an opportunity for material re-crystallization.
The findings from the current study suggest that the reported fluence values resulted in a laser-induced phase-change in the material from crystalline to amorphous. Whenever low energies are applied to the substrate by short pulses, heating of a thin surface layer results in a shallow liquid depth and rapid resolidification of the material does not allow for epitaxial re-growth [130-133]. This implies that Si atoms cannot rearrange again in an ordered, crystalline form. Instead, a disordered arrangement of Si atoms (some of them having dangling bonds) results in an amorphous layer. Liquid/solid interface velocities must be sufficiently high to promote amorphization from the melt and avoid crystal nucleation with typical values > 15 m/s for <100> Si [133-135] which are in agreement with the laser-fluence range used in this study. Considering this, the nano-bumps are generated when the laser intensity distribution is controlled in such a way that only the central part of the beam is above the material’s amorphization threshold. As the laser intensity increases above the ablation threshold, craters are formed at the centre of the beam while amorphous rims at their edges are created due to the Gaussian-profiled intensity distribution.

6.5 Conclusion

This work has reported the generation of nano-bumps of less than 2 nm in height on Si by a diode pumped Nd:YVO₄ laser system at 30,000 bumps per second. The formation of such bumps alters the wettability properties of the substrate. This effect is apparent as a difference in water droplet size when vapour condensation occurs on top of the material. By means of such difference, the laser marks made of such bumps can be visible without the use of complex equipment. This marking technique is debris-free, does not introduce contamination (apart from water vapour) to the material and could be implemented into practice straight away. X-ray photoelectron spectroscopy (XPS) analysis needs to be done in the future to determine the precise contents (i.e. at levels below one monolayer) regarding all the elements present on the surface samples before and after processing. This will give a better understanding of the wetting and de-wetting processes occurring on the surface of the laser marks. Also the technique could be explored for different applications including micro-fluidics and bioengineering.
Elliptical nano-bumps on nickel-phosphorous coated aluminium (NiP/Al) hard disks were fabricated by a laser texturing system (max. power of 8 W, max. frequency of 300 kHz). By carefully selecting the level of laser power attenuation and defocus offset distance, bump height can be controlled below 6 nm and down to the sub-nano metre scale. This type of laser-induced texture (elliptical shape) on a disk surface is expected to provide a better control of the stiction force along with the smallest separation distance between the head slider and the disk. Quantitative modelling based on the classical Hertzian theory for elliptic contacts has been carried out with the purpose of predicting the stiction behaviour of the presented elliptically shaped sub-10 nm bumps. It has been found that an elliptical shape not only reduces the overall stiction performance of the laser texturing zone (LZT) compared to the conventional circular shape but also extends the occurrence of the ‘stiction wall’ towards the sub-10 nm regime for ultra-low glide applications.
7.1 Introduction

In the hard disk drive (HDD) industry, increasing magnetic storage densities require an ultra-low flying height (below 10 nm, see fig 7.1), so that the head slider can perform the read/write operation [136, 137]. At storage densities greater than 10 Gb/in\(^2\), bump heights below 15 nm are necessary [138]. And if a 1 Tb/in\(^2\) aerial density is to be achieved, a head media spacing (HMS) of 6.5 nm is not only impending, but has already been established to go beyond a set of physical limits yet explored [137]. Inherent in the tendency for lowering the flying height, is the rise of some tribological issues such as a low glide resonance, less head-disk interference and a reduced stiction. To fulfill such requirements, a textured take-off and landing zone placed near the inner diameter of the disk should be carefully designed and generated [139]. Typically, the employed textures for this application are either a crater or a bump. Whatever the shape, a smaller cross-sectional area causes less perturbations during the slider’s motion. Moreover, it has been identified that this parameter which depends on the bump or crater width has the largest influence on the slider’s operating flying height [140].

![Figure 7.1 Basic components of a magnetic recording hard disk drive [139]](image-url)
Stiction is a critical tribological parameter during HDD operation. It is related to the adhesion tendency between two surfaces that are in close proximity. Therefore in order to overcome surface adhesion, a threshold force value is required. This is known as the stiction force, which in a hard disk must be very low so that the headslider can fly smoothly during take-off and landing operations without damaging the disk and the head. This value strongly depends on the texture characteristics of the landing zone such as bump shape, diameter, height, and distribution [141, 142].

Another tribological parameter that must be considered is the wear of the head-disk interface (HDI). This damage occurs due to the impacts during the contact start/stop (CSS) process, and surface texture can be adapted to minimize it [143]. It has also been established that in order to achieve the optimum surface texture that will reduce stiction and HDI wear, there must be a compromise between all the bump characteristics. However, it has to be remembered that the bump height is an imperative factor in the design of the flying conditions of the slider, as this determines the storage density of the magnetic disk.

Hard-disk laser texturing in the nano-metre scale has been successfully demonstrated by various authors [136, 142, 144-147]. Nevertheless, a very unique type of nano-bump with an asymmetrical profile has also been generated on a NiP/Al substrate. By scanning the beam along the lateral direction, elliptical bumps consisting of a peak on one side and a valley on the other have been textured on the disk surface. Several studies have acknowledged how this asymmetrical bump of elliptical contact area shows good wear durability, faster take-off/landing response, and lower glide resonance and stiction than the symmetrical circular crater shape [145, 148-152]. All the aforementioned conditions are critical for ultra-low flying head-disk interfaces (HDI’s).

In this chapter the outcome of texturing a NiP/Al disk by employing a commercial laser texturing system that delivers excellent repeatability and height accuracy control is presented. To be able to modify the shape, a rectangular mask was introduced in the optical setup. In this way, after a single pulse exposure, the bumps attain an elliptical shape that can be tested for low-flying height applications. The fabricated features exhibited an aspect ratio of ~ 2:1 (18 µm along the major
axis, 9.5 µm along the minor axis), and heights as low as 0.5 nm, with extremely high repeatability (± 0.4 nm). In addition, an improved mathematical model to predict nano-bump geometry on stiction characteristics has been employed. This is expected to aid the optimization of the laser nano-texturing process design and parameter selection for hard disk manufacture.

7.2 Laser Processing Experimental Procedure

Laser irradiation of a NiP/Al disk was carried out by a commercial diode pumped Nd:YAG LZT laser texturing system with the following characteristics: wavelength of 1064 nm, pulse duration of 82 nanoseconds, laser power of 8 W and a pulse repetition of 300 kHz.

This system is able to commercially produce bumps on NiP/Al disks with sub-nanometer accuracy and long term stability. These bumps can achieve 6-8.5 ± 0.4 nm heights, with a circumferential pitch of 16 µm (±1 µm) and radial pitch of 16 µm (±1 µm). This agrees well with the current industrial requirement of a standard deviation of less than 0.4 nanometres for the bump height and less than 0.2 micrometres for the bump diameter.

With a beam quality factor ($M^2$) of 1.04 and a beam diameter of 7 mm before focusing the beam onto the target by a single element lens ($f = 50$ mm), the calculated focused spot size on the disk is 10 µm. In this way, at 0.8 W and 300 kHz the energy per pulse delivered to the disk is 2.67 µJ which results in circular bumps having a diameter of the same dimension as the spot size. A metallic mask of 3 x 10 mm was placed before the lens to shape the beam spot from circular to rectangular (for optical setup see figure 4.2). A variable attenuator was used to control the laser fluence (pulse energy per spot area) delivered to the substrate.

By the adjustment of the laser parameters (i.e. laser power, focal position) and the introduction of the rectangular mask, the structures were modified from 6 nm high elliptical nano-bumps into sub-1 nm elliptical nano-bumps. The LZT laser
system enabled such sub-nano metre patterning on the material with the high precision of a few angstroms (1Å = 0.1 nm). The bumps exhibited a lateral size of 18 µm along the major axis and 9.5 µm along the minor axis with a periodicity of 17 µm.

Considering that a single pulse per bump was delivered and that the outer diameter (D_o) of the LZT band was set to 4.3 cm, 7505 bumps are to be textured during the first spin. As the laser operates at a frequency of 18x10^6 bumps/min, the starting spindle speed (ω_o) was set to 2398 rpm. In the same manner, an inner diameter (D_i) of 3.8 cm implied an end spindle speed (ω_i) of 2714 rpm for the process.

Regarding the linear scanning speed along the radial direction, the equation for the Archimedean spiral was helpful to define the radial dimension of the textured zone as:

\[ R = R_i + \frac{h}{2\pi} \theta; \]  \hspace{1cm} (7.1)

Where \( h \) is the step between each revolution and in the present case this corresponds to the bump periodicity of 17 µm, \( R_i \) is the inner radius of the spiral, and \( \theta \) is the angular position in radians. By obtaining the first derivative of (7.1) with respect to time as follows:

\[ \frac{dR}{dt} = \frac{h}{2\pi} \frac{d\theta}{dt}; \]  \hspace{1cm} (7.2)

It is possible to obtain an expression for the linear scanning speed of the process along the radial direction:

\[ v = \frac{h}{2\pi} \omega; \]  \hspace{1cm} (7.3)

According to this relationship, the starting linear speed (\( v_o \)) along the radial direction was 0.679 mm/s and the end linear speed (\( v_i \)) was 0.769 mm/s. The linear
scanning speed along the scanning (tangential) direction was 5.4 m/s. The production rate for this set of processing parameters is 6.9 seconds per disk. The processed samples were characterized by a high resolution (0.1 nm in the z axis) white light interferometer (Wyko NT1100).

7.3 Results

After laser texturing, a very distinctive shape was identified by the Wyko Optical Profiler.

![Figure 7.2 3D Optical profile image of elliptical nano-bumps arrays fabricated in the landing zone of a hard disk.](image)

It consisted of an elongated elevation in the material in the form of elliptical bumps, as shown in figure 7.3. These nano-bumps of an elliptical shape provide a minimized contact area without affecting bump density in the landing zone of a hard disk.
A closer examination of a 2D optical profile showed that these bumps present the typical “sombrero” shape across the minor and major axes. This implied a high protrusion in the centre of the bump (height: 6 nm ± 0.4 nm, diameter: 5 µm), a depression around this protrusion (height < 1 nm) and a smaller rim in the periphery of the bump (height < 1 nm). The overall diameter of the bump along the minor axis was 9.5 µm (figure 7.4) and 18 µm along the major axis (figure 7.5). In both measurements (i.e. major and minor axes) the surrounding depression and rim that accompany the main bump can be noticed in the optical profile image as an intense blue and a white “halo” respectively.
Uniform arrays exhibiting the aforementioned structures were readily obtained, as is shown in figures 7.6 and 7.7. Measurements showed a peak-to-peak periodicity of 17 µm across the minor and major axes of the bumps. However, due to the linking of the bumps across their major axis, the “sombrero” shape was lost as the bumps became joined together at their peripheral depression. It is noted that texturing is influenced by the roughness of the substrate (Rₐ: 0.2 nm) and even a small tilt of the plane surface can affect the topographic characteristics of these fine structures.
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Figure 7.7 3D Optical profile image of an arrangement of “sombrero” nano-bumps of circular shape.

The original “sombrero” bump with a circular shape (figure 7.8) is also presented here to show the topographical properties of this feature and how it can be modified into an ellipse in order to provide all the tribological advantages described in the introduction section. It is also confirmed how these bumps were designed to attain a height of 3.5 nm with a small deviation of only a few Angstroms (± 0.4 nm). Precision is critical and of great importance in order to fulfil industry demands for low-flying height (below 10 nm) in a hard disk application.

Figure 7.8 2D Optical profile of a circular “sombrero” nano-bump (height of 3.5 nm and diameter of 10.2 µm).
The 2D optical profile high “sombrero” bump is presented in figure 7.9. The bump height was 3.5 nm, whilst the diameter was 10.2 µm; an interesting feature is that the central bump is not accompanied by a surrounding “dip” or depression but by a smaller rim of approximately 1 nm in height. In the optical profile of the textured zone, the main bump is distinguished as a bright spot, whereas the surrounding rim exhibits a more subtle shade.

![3D Optical profile image of elliptical sub-nanometre bumps arrays fabricated in the landing zone of a hard disk.](image)

**Figure 7.9** 3D Optical profile image of elliptical sub-nanometre bumps arrays fabricated in the landing zone of a hard disk.

To further demonstrate the potential of the laser texturing system, bumps of sub-nanometre dimensions in the vertical scale were fabricated (figure 7.10). These bumps also followed the “sombrero” profile and elliptical shape of the first bumps described in this paper. They were differentiated from the surface roughness of the disk because the main bump protrudes above the original surface by a few angstroms (~ 0.5 nm ± 0.4 nm).
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Figure 7.10 2D Optical profile across the minor axis of an elliptical sub-nanometre bump.

Figure 7.11 also presents the typical surrounding depression of a “sombrero” bump, which in this case is also in the angstrom scale (~ 0.5 nm ± 0.4 nm). The total lateral size of the feature (including the surrounding depression) along the minor axis of the ellipse is 12.4 µm which is 3 µm larger than the 6 nm-high elliptical bump as reported earlier. This change in spot size might be explained by the defocus offset used during the experiments in order to attain a lower bump height [153].

Figure 7.11 2D Optical profile across the major axis of an elliptical sub-nanometre bump.

The 2D profile of the sub-nanometre bump across its major axis can be visualized in figure 7.12. The lateral dimension of the bump including the surrounding depression was 18 µm (in agreement with the 6 nm elliptical nano-bump
mentioned earlier) and its height measured from the original surface was 0.5 nm, which confirms the height measurement made across the minor axis. As can be seen from the 2 point profile, the surface of the bump appears to be quite rough, though it still has to be remembered that this is a consequence of the ultra-shallow height of the bumps that is on the same order as the original roughness of the disk (Ra ~ 0.1-0.2 nm).

![2D Optical profile of the central bump (height of ~ 1 nm).](image)

The height of the central bump measured from the bottom of the surrounding depression to the top was ~ 1 nm (figure 7.13) and its diameter was 6 µm. As reported in the literature, if the fluence value is further decreased, this central protuberance will keep reducing its height until an extremely small crater (of a few angstroms in depth) is formed. In these experiments this last feature was not achieved due to the fact that the bump’s height (which is already small enough) is what determines the purpose of the texturing technique for a low flying height application. Therefore, a crater without a rim around it was found to be of no use.

Naturally, this leads to the question: how small can the bump height be in order to still offer a competitive tribological performance? In order to assess this issue, a model was prepared to determine the benefits and possible limitations of the nanometre and sub-nm elliptical bump arrays fabricated in this work. Driven by an
ever-decreasing head-disk interface, modelling results are presented in the following section and compared to the conventional circular shapes.

7.4 Discussion

7.4.1 Nano-ridge formation mechanism

During laser irradiation, energy is absorbed by the material and a melt pool is formed when the melting point of the material is reached. Depending on the fluence delivered during the process, different convective fluxes arise inside the melt pool due to surface tension gradients (thermocapillary effects). Because of this capillary phenomenon, such fluxes trigger a “flush” movement in the melted material towards cooler areas of higher surface energy and when the cooling period starts and resolidification takes place, a permanent modification of the material becomes apparent in the form of a crater [154, 155]. However, chemocapillary effects [144, 156, 157] also play an important role in the final topography. They take place as surface composition gradients arise by temperature-induced vaporization of some species (e.g. phosphorus and oxygen). Areas of lower surfactant concentration have a higher surface energy, which implies that chemocapillary forces resulting from chemical composition gradients can be large enough to reverse the localized flow due to thermo-capillarity. Subsequently a “sombrero” or bump shape can be produced.

There are 4 main types of bumps that can be identified as a result of decreasing the fluence (energy per area) of a nano-second laser interacting with a NiP/Al disk and the subsequent competition between thermocapillary and chemocapillary effects. They are: a deep crater with a low peripheral rim, a double rim or “W” shaped crater (as the result of the centre of crater moving upwards), a central dome (or the “sombrero” shape) and a “bowl” like shape (this appears when the central dome has reduced its height until it disappears) [144, 155, 156].

Even though in this chapter there was a modification from a circular bump into an elliptical, the final topography of the bumps was in accordance with the aforesaid shapes. For example, the “sombrero” shape was clearly recognized in the
6-nm elliptical nano-bump and the sub-nm elliptical bump, for which the central dome extended along the major axis of the ellipse forming an elongated feature.

### 7.4.2 Stiction force modelling

To further study the effect of the elliptical shape and the reduced height of the bumps, mathematical modelling of the stiction force for elliptical Hertzian contacts was carried out. Liu and Li [148] investigated the stiction performance of tilted bumps (i.e. asymmetrical shape) by modifying an existing stiction model developed by Gui and Marchon [158] for regular and random textures that included the meniscus effect of a liquid lubricant.

The elliptical bumps introduced in the present work are not tilted but because of their constant streamline geometry their contact area can be considered to be elliptical. Therefore, by employing the modified model for elliptical Hertzian contacts adapted by Liu and Li [148], initial stiction performance was analysed and evaluated for elliptical bumps below 10 nanometres and in the sub-nanometre scale.

Hertz’s classic contact theory has been used to predict the stiction values for symmetrical sombrero or crater bumps in which the radius of curvature of the bumps limits the model to a one-dimensional case [159, 160]. However, an elliptical contact has to be examined as a two-dimensional problem in which there are 2 different radii of curvature corresponding to the major and minor axis of the ellipse (figure 7.14).
Figure 7.13 Schematic of the elliptical nanobump and its principal major and minor radii of curvature, \( R_x \) and \( R_y \), (a) corresponds to the base area of the bump whilst (b) refers to the contact area between the head slider (flat surface) and the elliptical bump.

The principal radii of curvature for the main axes of the contact ellipse can be calculated by considering the equation for the radius of a spherical cap:

\[
R_{x,y} = \frac{(H^2 + r^2)}{2H};
\]  

(7.4)

Where \( H \) is the height of the cap, and \( r \) is the radius of the base area of the cap. In the case of the nano/sub-nano elliptical bumps presented in this paper: \( H << r \), so the equation reduces to:

\[
R_{x,y} = \frac{r^2}{2H};
\]  

(7.5)

The equations that describe the stiction model for elliptical nano-bumps are presented as follow:

\[
S = \mu(W + F_m);
\]  

(7.6)

In which \( S \) is the initial stiction force between the elliptical contact and the head slider (flat surface), \( \mu \) is the coefficient of friction, \( W \) is the head load, and \( F_m \) is the total meniscus force. The latter is the result of a layer of liquid lubricant film
between the bump and the slider. The menisci formed around the contact points due to surface tension has an inside pressure that pulls both surfaces together and creates an additional normal force [158, 161]. The meniscus force can be expressed as:

$$F_m = P_m A_m = \frac{2\gamma}{h^2} \left( Ad_0 + N\pi R_1 R_2 h^2 \right);$$  \hspace{1cm} (7.7)

Here $P_m$ is the meniscus pressure, and $A_m$ the total area of the meniscus which can be calculated from the volume conservation of the lubricant under the effective area of the slider, $A$. $\gamma$ is the surface tension of the lubricant, $h$ is the elastically deformed bump height at rest, $d_0$ is the initial lubricant film thickness, and $N$ is the number of asperities under a slider.

By acknowledging the Hertzian contact theory, the total elastic contact force, $P_c$, between multiple elliptical bumps and a flat surface can be computed by:

$$P_c = \frac{4}{3} N E^* (H_r - h)^{1/2} (R_1 R_2)^{1/4} C^{-3/2};$$  \hspace{1cm} (7.8)

$$C = \left[ \frac{2}{\pi^2} \left(1 - \frac{R_2}{R_1}\right) \right]^{1/3} \left[ (\frac{R_1}{R_2}) E - K \right]^{-1/6};$$  \hspace{1cm} (7.9)

In (7.8), $E^*$ refers to the composite Young’s modulus of elasticity of the interface, and $E$ and $K$ are the complete elliptical integrals of the first and second kind for the eccentricity ($e$) or elliptical modulus ($k$) of the contact ellipse. The definition of the latter parameter is:

$$k = \sqrt{1 - \left(\frac{b}{a}\right)^2} ;$$  \hspace{1cm} (7.10)

Where $a$ and $b$ denote the major and minor semi-axes of the elliptical contact area.
In view of the following approximation [162, 163]:

\[
\frac{b}{a} = \left(\frac{R_y}{R_x}\right)^{2/3};
\]  

(7.11)

The complete elliptical integral of the first and second kind are defined as [164]:

\[
K(k) = \int_{0}^{\pi/2} \frac{d\theta}{\sqrt{1-k^2 \sin^2 \theta}}; \\
E(k) = \int_{0}^{\pi/2} \sqrt{1-k^2 \sin^2 \theta} d\theta;
\]  

(7.12, 7.13)

To complete the model, the meniscus force can also be expressed as the difference between the contact force and the head load:

\[
F_m = P - W;
\]  

(7.14)

The listed equations were solved numerically in Mathematica 7.0 software to obtain a model that will show the stiction behaviour of the elliptical nano-bumps as a function of their height, relative radii of curvature, and periodicity. Model parameters were set as follows: a lubricant’s surface tension of 25 mJ/m², an initial lubricant film thickness of 2.5 nm, an effective area of the slider of 0.5 mm², a composite Young’s modulus of elasticity of 100 GPa, a head load of 40 mN and a coefficient of friction of 0.2. All these parameters were taken from the literature and have been used by other authors in the stiction modelling of the textured take-off and landing zone of NiP/Al disks [158, 159]. The results reported here were found to be good in agreement with the ones obtained by Liu and Li [148].

As can be seen from the modelling graphs in figure 7.15 (a-b), an extremely small nano-bump height below 10 nanometres can result in very high stiction. This is
due to the fact that there is a minimum value in order for the bump size to have a significant influence in the laser texturing zone performance.

**Figure 7.14** (a) Stiction force (g) plotted against the height of an elliptical nano-bump of 9 µm along its major axis and 4.5 µm on its minor axis, (b) enlarged view of (a) for a bump height up to 15 nm. The insets show different periodicities and their corresponding symbols are identified in the stiction graphs.
Nevertheless, if the eccentricity ($k$) of the nano-bumps is varied (figure 7.16a), it can be observed that the initial stiction can be greatly reduced (~ 50%) for higher higher aspect ratio (i.e. a/b) elliptical shapes. It has to be remembered that the eccentricity of a circle is equal to zero, so when the elliptical aspect ratio of the bumps tends to a minimum and they appear more circular-shaped, higher stiction is expected. In figure 7.16 (b-c), modelling curves are presented for $k = 0.38$ and 0.5 which confirms that a more elliptical geometry implies better stiction results as the bump height is reduced.

The influence of the bump dimensions also plays an interesting role especially towards the sub-10 nanometre range. In figure 7.16 (b), it is seen that a bump with a dimension of 4.5 µm along its major axis is not suitable for a sub-10 nm
head-disk interface. But if the major axis dimension is set to be $> 9 \, \mu\text{m}$, a landing zone covered in these elliptical bumps is more appropriate for this application. However, the ultimate design goal will be to achieve smaller stiction values, which could be attained if the streamline geometry gets more elongated as dictated by $k \sim 0.50$. Figure 7.16 (c) shows the prediction results for such bumps, which appear to be more favourable for the present application.

Another factor that could be modified in order to improve the stiction performance of sub-10 nm bumps is the thickness of the lubrication film, which could be taken to a minimum of 0.8 nm as suggested by Gui [137].

From figure 7.16 (d) it can be concluded that reduced texture heights benefit from a thinner lubrication film. For example, if the film thickness is reduced to 0.8 nm an elliptical bump of 18 and 9 $\mu\text{m}$ along its major and minor axis can be designed to attain a height of 10 nm in order to achieve an initial stiction force of 1.7g. This value can be contrasted against 3g for the same bump characteristics but with a lubricant thickness of 2.5 nm. Similarly, an elliptical bump having an eccentricity of 0.5 (e.g. 18 and 1 $\mu\text{m}$ along its axis) is able to reach an initial stiction force of 0.6g for a 10 nm height bump. The height can be reduced further to 6 nm and the predicted initial stiction would be 1.7g.

These results indicate that the bump height can be aimed to a feasible minimum value if design parameters are carefully modified. According to their experimental results, Liu and Li recommended a 14 nm minimum height for an elliptical bump which could still show acceptable tribological performance: an experimental maximum stiction coefficient of 0.6g (their modelling results showed higher values of 1.2g for the same height). The current modelling results suggest that, a reduced height of 10 nm could also provide an initial stiction of 0.6g if the eccentricity was adapted to 0.50 and the lubricant thickness reduced to 0.8 nm.
By comparing the stiction performance of elliptical sombrero and circular crater shapes [159] it was found that the elliptical nano-bumps represent a more advantageous solution for the stiction performance of low glide interfaces. This can be appreciated in figure 7.17, in which the lowest height for a conventional circular crater (8 µm diameter) is 14 nm whilst the lowest height for an elliptical bump (18 µm and 9 µm along its principal axes) is 9 nm.

These results indicate that elliptical bumps are not only adequate for the sub-10 nm ultra-low flying height demanded by the hard disk industry, but yield to much lower stiction values than the conventional circular shapes even if a lubricant film thickness of 2.5 nm is considered. They also suggest that lower lubricant thickness values (e.g. 0.8 nm) will significantly decrease the initial stiction force (e.g. 2.3g for an 8 nm elliptical bump) and further extend the landing textured zone into the ultra-low flying height region (<10 nm), see figure 7.16 (d).
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Undoubtedly, an elliptic geometry is more favourable than a circular one for a laser textured zone application. However, it is interesting to note that for bump heights below 5 nm the theoretical limit in their stiction performance becomes a design challenge. An imminent “stiction wall” for extremely low heights means that fabricating ultra-low regular bumps, though feasible, might be detrimental for the present application if the design parameters are not fine-tuned. So, the current goal does not only require the fabrication of the lowest bumps (as demonstrated in the results section) but also the design of a precise geometry (i.e. elliptical shape with a eccentricity value towards 1) and to consider other factors that might be influential in the head media spacing (HMS) limits, such as disk/head overcoat and lubricant film thicknesses.

7.5 Conclusion

A regular array of nano-structures on a NiP/Al disk is reported. Their elliptical shape (in the form of narrow, elongated ridges) is expected to enhance the overall tribological characteristics of the landing zone [150]. The reported nano and sub-nano scale elliptical bumps possess a favourable geometry that could be tested for low-flying performance, including: stiction, glide resonance, head-disk interference, take-off/landing response and durability in contact start/stop tests. At a production rate of 6.9 seconds per disk, another novel feature of this type of bumps is that they can be designed to attain sub-nano metre height if required in order to meet industry requirements. The close relationship between stiction and wear performance [138] and the ever-decreasing head-media spacing prompted the stiction modelling in this work based on Hertz’s classic contact theory for elliptical contacts. The obtained results may be used in the tribological optimization of surfaces that are in close proximity and relative motion (e.g. MEMs, sliding mechanical contacts). The model can also be applied to other kinds of substrates (i.e. glass, metals) and other applications in which stiction and wear are crucial concerns.
A practical approach to a well known technique of laser micro/nano patterning by optical near fields is presented. It is based on surface patterning by scanning a Gaussian laser beam through a self-assembled monolayer of silica microspheres on a single-crystalline silicon (Si) substrate. So far, the outcome of this kind of near-field patterning has been related to the simultaneous, parallel surface-structuring of large areas either by top hat or Gaussian laser intensity distributions. The present work explores the possibility of using the same technique in order to produce single, direct writing of features instead of massive patterning. This could be of advantage for applications in which only some areas need to be patterned or single lines are required (e.g. micro/nano fluidic channel).

A diode pumped Nd:YVO₄ laser system (wavelength of 532 nm, pulse duration of 8 ns, repetition rate of 30 kHz) with a computer controlled 3 axis galvanometer beam scanner was employed to write user-defined patterns through the particle lens array on the Si substrate. After laser irradiation, the obtained patterns which are in the micro-scale were composed of sub-micro/micro holes or bumps. The
micro-pattern resolution depends on the dimension of both the microsphere’s diameter and the beam’s spot size.

In order to compare the pulse duration effect on pattern dimensions and surface finish, a femtosecond laser source (Ti:Sapphire Libra-S System, \(\lambda: 800\) nm, \(\tau: 100\) fs, \(f: 1\) kHz) was used to scan over the lens array on Si. In general, surface quality was greatly improved; moreover, laser induced periodic surface structures were found near the laser fluence threshold for fs irradiation. This observation is reported for the first time.

The developed technique could potentially be employed to fabricate photonic crystal structures mimicking nature’s butterfly wings and antireflective “moth eye” arrays for photovoltaic cells. The main advantage is that this could be done in custom-designed areas/shapes, with a resolution limited only by the micro-sphere size.

8.1 Introduction

In recent years an increased interest in replicating natural behaviours (also known as biomimetism) has attracted a lot of research effort [165, 166]. Research on the micro-nano structure of butterfly wings has shown them as natural photonic crystals. This has established a strong link between the vivid wing colours and the morphology of the wings [167]. Insects use light manipulation as a means to signal between one another but also for thermoregulation and camouflage purposes. The object of such recent interest on natural photonic structures has its roots in the engineered design by which living organisms manipulate and control light to fulfil specific needs [168]. Structure periodicity dictates the way light behaves when encountering a surface (i.e. reflection, absorption and transmission). To be able to control light in the optical spectrum, structuring of materials has to be done within the same scale typically ranging from hundred nanometres to several micro-meters.
Dimensions of periodicity (1D, 2D or 3D) affect the electromagnetic band gap of the material in the visual wavelength range [169], which could change surface colour or form anti-reflective surfaces. These surfaces are known as “moth eye”, “nipple arrays” or “subwavelength structures (SWS)” [170-175]. In nature they appear in the eyes of some insects helping them to enhance the photon collection of their visual system and to reduce reflection that could attract predators.

Vukusic found recently that nanostructures on the wing scales of some butterflies enhance optical absorption by 90 to 95% resulting in enhanced black colouration [176]. The explanation for such an effect is attributed to the effective medium theory which states that a subtle change in the optical impedance between two mediums will reduce Fresnel reflection. Many micro and nano-fabrication techniques could fulfil the challenge of fabricating photonic structures in a diversity of materials [22, 24, 27, 45, 77, 89, 177-182]. In the long term, only the most economic and feasible ones will prevail as the accepted method of fabrication.

This chapter aims to demonstrate how a widely-recognized near-field nano patterning technique could be used to fabricate custom-defined, single-line micro/nano structures, or to create 2D photonic structures in delimited areas exhibiting distinct shapes (i.e. curves, lines, spiral forms, letters) instead of simultaneously patterning millions of features over large areas as it has been done until now. This novel approach is presented in this chapter based on the “Contact Particle-Lens Array” technique which relies on the near-field enhancement effect by small particles interacting with a laser beam.

### 8.2 Theory

In the Contact Particle-Lens Array (CPLA) technique, a particle mask consists of a self-assembled monolayer which offers massive, parallel nano-structuring with a significant improvement in patterning speed under single laser pulse radiation [54, 183-186]. This near-field patterning mechanism was first identified after surface damage appeared during the process of particle removal by
dry laser cleaning (DLC) [187, 188]. The technique was further developed by many authors who have studied the near-field effects of small particles on a substrate when subjected to laser irradiation [189-194]. Transparent spherical particles which compose the monolayer are used as a lens array for focusing far-field laser radiation. The near-field lens array produces a strong field enhancement at each particle-sample contact point. Due to the involvement of evanescent waves, the near-field foci can be scaled below the diffraction limit [54, 58] i.e. super-resolution effect.

Figure 8.1 Cross sectional view of the normalized local field distribution: (a) $|E|^2$; (b) $\text{Re}[S_z]$ underneath a 5 $\mu$m SiO$_2$ microsphere in air (incident laser beam of wavelength $\lambda = 532$ nm, pulse duration of $\tau = 8$ ns).

In order to show the basic physics of the near-field focusing effect induced by a small particle, Mie’s theory modelling of the optical near field around a single particle was carried out. Figure 8.1 shows the modelling results in a cross sectional view of the normalized local intensity field distribution (normalized electric field intensity $|E|^2$ and the real part of the z-component of normalized Poynting vector $\text{Re}[S_z]$) underneath a particle (diameter of 4.74 $\mu$m, refractive index of 1.45) in air.
when subjected to an x-polarized plane wave excitation at a wavelength of 532 nm, and pulse duration of 8 ns.

By comparing figs. 8.1(a-b), one can clearly see that the field distribution of $|E|^2$ differs from the $\text{Re}[S_z]$ field distribution. The difference, again, arises due to the presence of the evanescent wave components in the near-field regions.

From the same figure, it can also be seen that the focus point for such a particle (in air) is at a position $z/a = 1.2$ ($a$: particle radius); very close to the particle surface. It can also be seen that the near-field enhancement decays to half its maximum in the range from $z/a = 1.2$ to $z/a \sim 1.455$ which means that a sample must be kept in near-field distance with the particle lens array for efficient patterning. It should be noted that the current simulation is limited to the simplest case of a single particle subjected to laser irradiation based on classical Mie theory. To include influences of substrates and neighbouring particles on the focusing and near-field distributions, extended numerical modelling techniques have to be used. This approach along with detailed information on optical near-fields in different particle-substrate systems (particle aggregates, particle on substrate, particle in solution, etc.) has been reviewed in a recent papers [195].

8.3 Experimental

8.3.1 Nanosecond laser irradiation

The experimental setup is portrayed in figure 8.2(a). The sample used is a p-type single-crystalline Si wafer, <100> orientation, boron doped with resistivity of 1-10 $\Omega \cdot \text{cm}$. A diode pumped Nd:YVO$_4$ laser system (Laservall Violino, $\lambda$: 532 nm, $\tau$: 8 ns, f: 30 kHz) was employed as the light source. A computer-controlled three-axis Galvanometer beam scanning system is attached to the laser system, allowing fabrication of arbitrary patterns on the sample surface.
Chapter 8-Micro/Nano-Scale Patterns by Nd:YVO4 Laser scanning over Particle LensArray

Figure 8.2 Schematic views of: (a) experimental setup; (b) focused laser beam scanned over the SiO2 monolayer (to scale: 5 μm diameter SiO2 micro-sphere); (c) scanning electron micrograph (SEM) of a self-arranged monolayer formation of 5 μm SiO2 micro-spheres.

In the experiments, the samples were first cleaned with acetone and methanol, followed by a de-ionized (DI) water rinse and then dried. A drop coating method was then utilized to deposit a uniform monolayer of silica (SiO2) microspheres onto the sample surfaces. After this a hexagonal array of particles was formed by a self-assembly process where the quality of the monolayer depends on many factors such as the cleanliness of the surface, wettability, temperature and any environmental disturbance. The obtained monolayer mask in these experiments is shown in fig. 8.2(c), and was in reasonably good quality over a large surface area. The non-porous SiO2 microspheres (refractive index of ~ 1.43-1.46, mean diameter of 4.74 μm) utilized in these experiments were initially buffered in DI water with a 9.8 (wt %) solids content.
Figure 8.3 Optical micrograph of a micro-spheres monolayer after laser irradiation by a focused Gaussian beam. SiO$_2$ micro-spheres remained in the surface on top of the generated sub-micro/micro structures which explains the change in reflectivity. Also shown is the site were a micro-sphere was removed leaving a hole behind (shown inside the circle).

The prepared samples coated with particles were then scanned with a Gaussian laser beam as shown in fig. 8.2b. The laser focus was of elliptical shape with a spot size of ~ 50 µm along the minor axis and ~ 80 µm along the major axis. The applied laser fluences were set below the ablation threshold of bare Si in the reported experiments. At laser fluences below ~ 200 mJ/cm$^2$, no apparent material modification takes place on a bare surface. However, due to the field enhancement effect given by the particles, ablation took place at the sites where microspheres were located, see figs. 8.3 and 8.4. In this way, arbitrary patterns of width in the same scale as the beam size are composed of sub-micrometer structures due to the combination of the conventional laser direct micro-fabrication technique and the CPLA technique. To the best of the author’s knowledge, such a kind of double-scale texturing (i.e. micro-sized patterns made of sub-micron and/or nano-structures) was reported for the first time. Though in the past several authors detailed the use of a focused Gaussian beam to irradiate micro-spheres in order to produce parallel nano-patternning in a variety of substrates [196-198], the present work demonstrated the use
of a focused beam to scan across a monolayer formation in order to obtain single patterns instead of massive, parallel structuring.

In the experiments the pulse repetition rate was set as 30 kHz and the scanning velocities were varied from 1000 to 5 mm/s which resulted in multiple pulses being delivered to each spot for the lowest velocities. Although most of the particles can be removed after a single pulse irradiation, it was noticed that for the lowest fluence applied (150 mJ/cm$^2$) some particles remained on top of the sub-micro-structures possibly due to a small tilt in the scanning beam path. This can be seen in figure 8.3 in which a variation in reflectivity is present in the locations where the Gaussian beam was scanned. The rest of the particles that remained in the areas where the laser beam was not scanned, were removed after the process by sweeping a lens cleaning tissue over the surface. The processed samples were characterized by employing an Optical Microscope (OM, Polyvar MET), a Scanning Electron Microscope (SEM, Hitachi S-3400N) and an Atomic Force Microscopy (AFM, Veeco Innova Scanning Probe Microscope).
Figure 8.4 SEM images of micro-scale lines made of sub-micrometre structures generated after a focused Nd:YVO₄ laser was scanned over a 5µm spheres array: (a) fluence of 200 mJ/cm², scanning velocity of 5 mm/s, line width of 72 µm; (b) fluence of 170 mJ/cm², line width of 53 µm; (c) fluence of 150 mJ/cm², line width of 34 µm; (d) fluence of 150 mJ/cm², scanning velocity of 100 mm/s, line width of 24 µm; (e) fluence of 150 mJ/cm², a scanning velocity of 1000 mm/s (1 m/s) results in the individual mark for each pulse per spot; (f) fluence of 150 mJ/cm² might also generate amorphised nanobumps (white spots).

The patterns shown in figure 8.4 (a-c) were generated by the above described technique at laser fluences of 150-200 mJ/cm², a scanning velocity of 5 mm/s and a
laser repetition rate of 30 kHz (this implies a delivery of 300 pulses per spot). The contrast between the laser scanned lines and the bare substrate is given by the scattering effects of the different generated sub-micro/micro metre structures. The width of the laser-scribed lines at a fluence of 200 mJ/cm² is ~ 72 µm and descends to 34 µm at a fluence of 150 mJ/cm². Further reductions in width are observed in figure 8.4(d) if the scanning velocity is increased to 100 mm/s (15 pulses per spot) which results in a 24 µm line (formed by about 5 sub-micro structures across the minor axis of the beam), this is smaller than the laser spot size of 50 µm x 80 µm.

Due to limitations of the current system it has not been possible to decrease the far-field focal spot size so only a single line of particles is irradiated, but work is being undertaken in order to further reduce such a parameter. Shown in figure 8.4(e) is the effect of scanning only one pulse per spot in the monolayer formation, where the elliptical shape of the beam is clearly appreciated.

8.3.3 Femtosecond laser irradiation

A Ti:Sapphire femtosecond laser source (Libra-S system, λ : 800 nm, τ : 100 fs, f: 1 kHz) was utilised to scan a 5 µm SiO₂ monolayer. The physical processes involved in the interaction of femtosecond pulses with a Si substrate, along with the formation mechanisms of surface structures in this pulse regime will be explained in chapter 9 of this thesis. Nevertheless, the obtained micro/nano patterns obtained from scanning the femtosecond Gaussian beam gave similar results as the nanosecond laser. The difference was found in the surface finish of the patterns which was improved for the femtosecond case; and the presence of periodic ripples characteristic of ultra-fast irradiation with some materials at low fluences, near the ablation threshold. These ripples have a dimensions and periodicity in the nanoscale and will be thoroughly studied in the next chapter.
In figure 8.5, a set of SEM images exhibiting the results of scanning a femtosecond laser over a particle lens array are presented. The applied fluence was 0.19 J/cm² at a scanning speed of 1 mm/s. The spot size was also elliptical (x: 75 µm, 96 µm), so 75 pulses per spot irradiated the lens array. Just as with nanosecond pulses, particles were removed after single pulse fs irradiation.
In figure 8.5(a), the sections scanned are indicated by arrows. Areas of the monolayer that were not affected by laser irradiation are clearly identified as micro-spheres were left in their original location (fig. 8.5b). The two insets marked in figure 8.5b correspond to the enlarged views of fig. 8.5(c-d). The central part of the scanned line where intensity is at its highest was populated by nano-craters generated by the near-field enhancement of the laser scanned particles. Additionally, ripples formed all over the scanned surface for which the Gaussian beam intensity was enough to induce this type of self-organised structuring. The outcome was a double-texture patterning of nano-craters and nano-ripples (fig. 8.5c). At the edges of the beam, laser intensity is not enough to trigger ripple formation, however the near-field effect was sufficient to produce nano-craters (fig. 8.5d).

Interestingly, periodicity of the ripple structures was found to be ~ 560 nm (fig. 8.5e), and the nano-craters created simultaneously presented diameters close to 500 nm. This contrasted with the periodicity (~ 660 - 770 nm) of ripples formed in bare Silicon without any particle lens array. Also the nano-craters formed outside the nano-rippled area, showed a larger diameter, up to 1 µm. These findings suggest that a change in the refractive index of the first medium (i.e. from air to SiO$_2$) could have been responsible for the variation in ripple periodicity. Such an observation will require further study in order to determine the cause of such a decrease in dimension and periodicity.

When the laser fluence was decreased to 0.14 J/cm$^2$, the ripple effect was also reduced, see fig. 8.6 a-b. From these SEM images, it is appreciated that ripples occurred only at the central part of the scanned lines, and in an intermittent manner. Nevertheless, the presence of nano-craters dominated the scanned surface. This was more evident when the fluence was further decreased to 0.14 J/cm$^2$ (fig. 8.6c). As it will seen in chapter 9, below 0.12 J/cm$^2$, ripples are still formed for multiple pulse irradiation on bare Si, but no visible material modification occurs in the single pulse regime. However, the intensity given by the particle lens array allowed for material ablation at the nanoscale with good surface finish. A 16.2 µm line was obtained at 0.09 J/cm$^2$ (fig. 8.6d), but if a tighter spot is employed finer lines could be made.
8.4 Discussion

The decrease in sub-micro structure size in the lateral edges of the laser-scribed lines seen in all the SEM images of figure 8.4 occurred due to very low fluences beneath the peripheral micro-spheres irradiated by the Gaussian beam. Such low fluence values also resulted in the amorphisation of Si under the micro-spheres at these particular edges. The characteristic “white” halo structures seen in amorphized Si [109, 110, 199] are presented in figure 8.4(f).

The AFM image in fig. 8.7 (a) clearly shows the different surface morphologies of ablated sub-micro structures by a focused Gaussian beam. A change in the height profile according to the laser distribution is clearly defined from the outer part towards the central part of the beam, where structures are at their highest because of the accumulation of molten material in the form of a bump of ~ 250 nm
height. On the contrary, structures formed at the edges of the Gaussian distribution manifest bumps of height ~ 10 nm height and craters of depth ~ 10 nm.

A more accurate profile dimensional analysis was performed for different morphologies and their different profiles are shown in figure 8.7 (b-d), where it can be observed that craters, bumps and “sombrero” shapes can be found across the major axis of the elliptical spot. The larger structures (craters with significant debris around them and bumps formed by debris accumulation) were formed when the central part of the beam was scanned over the contact particle lens array. Their formation is clearly related to the near field enhancement given by the contact particle lens array when irradiated by the laser beam.
Figure 8.7 (a) AFM image of a micro-scale line formed by sub-micrometre structures and the respective height profile across the width of the line; (b-d) Different height profiles of some of the structures found along the beam’s intensity distribution.
Considering the laser intensity near-field enhancement under the micro-spheres and the employed nanosecond laser, photo-thermal ablation in the form melt-expulsion/redistribution could be acknowledged as the material removal mechanism in this process [97-99]. Smaller bumps like the one shown in figure 8.8 can be found in the periphery of the ablation spot, the formation mechanism in this case is different and can be explained by a lower intensity enhancement that can cause convective fluxes inside the melt pool due to surface tension (thermo-capillary effect) [129].

Different computer designed patterns could be easily transferred to the samples by utilizing the integrated galvo-scanning system. The obtained results are shown in figure 8.9 (a-d), where a high contrast in the images is given by the optical scattering effects of the laser-generated sub-micro/micro metre structures described above. This patterning technique is intended to be further developed in order to decrease the line lateral dimension by employing a tighter spot size and smaller microsphere diameters.
Figure 8.9 (a-d) Laser-scribed patterns made of sub-micrometre structures when a focused laser beam was scanned over a 5 μm SiO₂ monolayer at a fluence of 170 mJ/cm². Patterns are visible due to the optical scattering effects of the sub-micro/micro structures.

Figure 8.10 SEM micrograph of a self-assembled monolayer of SiO₂ micro-spheres and the proposed scanning path of a focused beam in order to fabricate micro/nano arbitrary patterns by employing the CPLA technique.
In figure 8.10, the ideal scanning path of a focused beam over a pre-defined pattern is portrayed and it could be made possible if the spot size is further reduced so only a single micro-sphere is irradiated by a single or multiple pulses. This could lead to the production of lines or features made of nano-structures assuming that the correct parameters are selected (i.e. fluence value, micro-sphere size).

Moreover, by consecutively changing the angle at which the beam reaches the micro-spheres array and by delivering several pulses at the same location, continuous lines with a lateral dimension below the diffraction limit could be generated by connecting several ablation sites under the same micro-sphere. So far this technique of using an angular laser scanning beam over a self-assembled monolayer has been used to produce millions of arbitrary-shaped nano-patterns in a parallel manner [62], but it could be further extended to obtain only single lines or patterns if a tight focus spot is employed to irradiate fewer or only one microsphere along its scanning path.

The sub-micro/micro structures obtained in this chapter can be refined to attain specific dimensions in diameter, depth, shape, and periodicity so they can be used as antireflective surfaces for solar-cell applications or as photonic structures with a structural colour function to be employed as pixels in reflective colour displays [200]. More applications include the fabrication of single nano-channels and soft-marking of materials in which size of marks is crucial.

8.5 Conclusion

This chapter has presented an extended application for a near-field laser nano-fabrication technique that combines conventional direct laser micro-processing and a particle-assisted laser nanofabrication technique to generate micro-patterns that are composed of sub-micrometer/micro structures. This was demonstrated by rapid scanning a focused Nd:YVO$_4$ laser beam over a self-assembled particle lens array of SiO$_2$ microspheres on top of a Si surface, however more work needs to be undertaken in order to produce finer micro/nano patterns.
Also, scanning with a focused Ti:Sapphire femtosecond laser beam was proved to be of use to achieve better surface quality nano-craters. The generation of ripples at a specific wavelength range was also demonstrated in the experiments carried out in this chapter. The double texturing produced by the combination of fs pulses and CPLA showed a decrease in nanostructuring dimensions and period. The explanation for this will require further study; but at a first glance, the scanned areas exhibited signs of structural colour. This specific application will be presented in Chapter 10 of this thesis.

The obtained sub-micrometer patterns have the potential to replicate natural photonic crystals, such as “moth eye” and “butterfly wing scale” structures.
CHAPTER 9

FEMTOSECOND LASER FABRICATION OF SELF-ASSEMBLED NANOSTRUCTURED PERIODIC ARRAYS ON SILICON

Laser induced periodic surface structures (LIPSS), known also as ripples because of their wavy-like topography, exhibit periodicity in the range close to the incident laser-wavelength with a ripple orientation perpendicular to the electric field \( \vec{E} \). They are the result of interference between laser light and surface electromagnetic waves, when the energy deposited in the material is near the ablation threshold. Below such a value, no ripples are found for single pulses. In this work the outcome of employing a femtosecond laser to structure Si surfaces by single and multiple pulses is presented. The works shows that the ripple formation threshold for the multiple-pulse regime is lower than the threshold for single-pulse irradiation, which can be explained by an energy incubation effect as suggested by other authors. The possibility of a chemical incubation effect is considered based on our observations of a change in wettability of scanned areas by single and multiple femtosecond pulses.

9.1 Introduction

Several theories have been proposed for LIPSS formation mechanism, Sipe et al.’s [201] explanation being the most referred to in the literature. After their account,
it has also been suggested that for femto-second irradiation, Surface Plasmon Polaritons (SPP) may have a large influence in the creation of the Surface Electromagnetic Wave (SEW) which interferes with incident light producing energy spatial modulation and consequently localized modulated ablation [202, 203].

The outcome of this periodic distribution of energy is the formation of ripples which due to their periodical spacing not only resemble in a fascinating way the morphology of the nano-structures found in the scales of the butterfly wings but also show the same iridescent interaction with incoming light. It is the intention of this work to show the evolution of these nano-structures in single-crystalline silicon by a femto-second laser source from higher-order hierarchical structures (i.e. micro-channels, micro-holes and micro-columns) down to nano-structures (i.e. nano-ripples and nano-holes). It is demonstrated that the formation mechanisms are different for single and multiple pulse irradiation. An incubation effect is regarded as the cause for ripple formation below the ablation threshold. Vapour condensation is observed in areas irradiated by multiple pulses below the ablation threshold, which might suggest a change in surface energy of the first layers of the material.

9.2 Experimental Setup

A femto-second chirped pulse amplification system (Libra-S, diode pumped Ultrafast Ti: Sapphire) was employed to process the surface of <100> single crystal Si wafers. The samples were processed in air conditions and perpendicular to the incoming Gaussian beam, at a repetition rate of 1 kHz, with an average laser power of 1 Watt. The laser wavelength was centred at 800 nm, and the pulse duration was 100 fs. Due to an astigmatic lens, the focused spot size as measured from ablation sites by scanning electron microscopy was slightly elliptical with a diameter of \(~96\) and \(75\ \mu m\) along the major and minor axes, respectively.
Figure 9.1 Femtosecond laser system experimental Set-up.

In order to control the laser fluence and the orientation of the electrical field, a neutral density filter wheel and a half-wave plate were placed in the optical train before the beam was directed into a galvo-scanner head. A schematic of the optical set up is presented in figure 9.1.

As the pulse frequency was fixed at 1 kHz, the number of pulses per spot was controlled by the scanning speed. In the experiments, this value was incremented from 0.1 to 250 mm/s resulting in different surface morphologies for the same fluence value at different pulses per spot. A power meter measuring the power of the beam just before entering the galvo-head read fluences from 17 J/cm$^2$ (maximum average power) down to 0.078 J/cm$^2$. The combination of these processing parameters resulted in a variety of surface structures from nano-meter sized ripples and holes up to deep micrometre craters. Surface modification was characterised by means of a Scanning Electron Microscope (SEM, Hitachi High Technologies S-3400N).
9.3 Results

Femto-second machining of Si has been preferred over other methods due to the non-thermal ablation characteristic of ultra-short pulses. In this type of interaction the absorption of laser light excites the electrons in the conduction band even when the pulse duration finishes well before the electron-phonon coupling. As the dielectric function of Si changes, a surface electromagnetic wave (SEW) is generated and exists only for the duration of the fs laser pulse. After thermalisation of non-equilibrium electrons, the SEW fingerprint is responsible for the ripple formation due to its interference with incident laser light (i.e. from subsequent fs pulses) [202, 204]. Although ripples, holes and columns have all been identified as a result of the near-ablation threshold interaction between femto-second laser pulses with Si [205-208], it is observed in this chapter that the initial surface modification is different for single and multiple pulses irradiation.

9.3.1 Multiple pulses irradiation at high fluence (> 5 J/cm²) irradiation: No rippling

Surface modification of Si for the maximum fluence available from an average power of 1 Watt at two different scanning speeds is presented in figure 9.2. This implied a different number of pulses per spot and also significant pulse overlapping. This had an effect not only on the morphology of the micro-structuring but also in the depth and amount of re-deposited material around the structures.
Figure 9.2 Surface modification of Si by femto-second laser processing at: (a) 17 J/cm², 0.1 mm/s (750 pulses per spot); (b) 10 mm/s (~ 8 pulses per spot).

For example, for a scanning speed of 0.1 mm/s, the calculated pulse per spot number is 750, which as can be seen in figure 9.2(a) produced a deep trench along the scanning direction with a significant amount of debris along the edges of the channel which a extended the lateral dimension up to 130 µm. When the scanning speed was increased to 10 mm/s, only ~ 8 pulses were delivered to the same spot, and it is clear from figure 9.2(b) that material re-deposition around the edges is eliminated which decreased the measured lateral size to ~ 98 µm.

As the scanning speed was increased, it was possible to identify more clearly the overlapping of pulses that made up the channel and also the way material was ejected after each pulse deposition. This formation mechanism can be regarded as explosive ablation where material was ejected/splashed from the surface due to an overheated surface layer [209, 210].

9.3.2 Multiple pulses at 5-0.6 J/cm²: First signs of fine rippling

Below 5 J/cm² and down to 0.6 J/cm², a different surface modification was observed. When ~ 750 pulses per spot were applied (scanning speed of 0.1 mm/s) at 2.2 J/cm², the channel did not present significant re-deposition of material on its edges or in the near periphery (fig 9.3a) in contrast to the machined channels at
higher fluences. As the fluence was reduced by almost an order of magnitude (0.6 J/cm$^2$), the morphology at the centre of the channel resembled a combination of deep excavated micro-holes with nano-rippled walls (Δ~ λ) (fig. 9.3b). On the outer edges of the channel, micro-ripples were evident, formed probably due to an incubation effect triggered by multiple pulses at the low fluence edges of the Gaussian beam.

Figure 9.3 Surface modification of Si by femto-second laser processing at: (a) 2.2 and (b) 0.6 J/cm$^2$, and scanning speed of 0.1 mm/s (750 pulses/spot).

Figure 9.4 Surface modification of Si by femto-second laser processing at 0.6 J/cm$^2$: (a) 1 mm/s (75 pulses/spot); (b) 10 mm/s (~ 8 pulses/spot).

These first signs of rippling at this fluence regime can be better understood for channels formed with less pulse overlapping. For 75 pulses per spot (fig. 9.4a) no micro-holes are formed, however the bottom of the channel is covered by an accumulation of microstructures and the outer edges of the channel exhibited fine ripples (~ 700 nm) perpendicular to the electric field from incident light (see inset of
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The formation mechanism of these microstructures has been previously identified as a nucleation growth process that evolves from initial defects (e.g. surface defects, corrugations, rippling), with material ablation taking place at the valley and top points of these surface defects. As material re-deposits at the top of the structures, with an increased number of pulses, the protrusions grow accentuating the effect by an incident light trapping mechanism between their walls [210, 211].

For less than 10 pulses (fig. 9.4b), surface modification is characterised by splashed material around the irradiated spot, which is not different from the formation mechanism at higher fluences (i.e. phase explosion) however, the apparition of fine ripples on the edges (see inset of fig. 9.4b) indicates that fluence values on the outer edges of the Gaussian pulse is enough to prompt the formation of the first signs of LIPSS.

Figure 9.5 Surface modification of Si by femto-second laser processing at 0.4 J/cm$^2$ and scanning speed of 0.1 mm/s (750 pulses per spot).
9.3.3 Multiple pulses irradiation at: 0.5–0.3 J/cm²: Hierarchical structuring

The ripple effect starts to take larger significance at a lower-fluence regime which can be said to start at 0.3 J/cm². At this stage, for multiple pulse fabrication, the presence of large micro-holes declined; and extending towards the edges of the channel, micro-holes were eventually replaced by an array of micro-column structures oriented parallel to the incident electric field vector. So in the same laser-fabricated channel, 3 different hierarchical structures were clearly distinguished: ripple-walled micro-holes, micro-columns and ripples, these last two were oriented perpendicular to each other (see fig. 9.5 insets).

Such a combination of micro and nano-structuring may help to explain higher-order structures. For example, due to the Gaussian distribution of the incoming beam, power attenuation at its edges produced low-spatial material modification in the form of ripples. As higher power is concentrated towards the centre of the beam, it could be said that overlapped pulses enabled the formation of perpendicularly superimposed column-like structures on top of the original ripple ‘fingerprint’. At the centre, where power is at its highest, deep micro-holes with their walls covered in nano-ripples are generated which can be explained by an interference effect and localised ablation, accentuated by a low-fluence inter-pulse feedback mechanism.

This indicates that the initial rippled modification of the material might have served as a mould for consecutive pulses that shaped the material accordingly into higher order structures. This can also be visualised in figure 9.5 as the superimposed columns were ‘weaved’ by a scaffold of underlying ripples in a nucleation growth process, as previously mentioned.

9.3.4 Multiple pulses irradiation at: 0.4–0.09 J/cm²: Ripple origins

For fluences between 0.4 and 0.09 J/cm², ripple formation is predominant which can help to explain the earliest stage of their formation mechanism. At low
scanning speed (0.1 mm/s) and 0.2 J/cm$^2$, micro-holes are no longer present, but rather micro-columns populate the center of the channel with rippling occurring towards the sides of the channel (fig. 9.6a).

Irradiation by multiple pulses appeared to intensify the interference effect triggered by incident light and a surface electromagnetic wave. Further pulses will encounter an initial pattern and if more energy is delivered to the same spot, the effect gets accentuated and larger structures will form in the same sites that were initially modified (fig. 6b). Most likely, if fluence is reduced below 0.19 J/cm$^2$, micro-columns will disappear and the channel would be formed only by ripples provided that enough pulses are delivered to the material.

**Figure 9.6** Surface modification of Si by femto-second laser processing at: (a) 0.19 J/cm$^2$, 0.1 mm/s (750 pulses/spot); (b) 0.5 mm/s (150 pulses/spot); (c) 10 mm/s (8 pulses/spot); (d) 0.09 J/cm$^2$, 10 mm/s;
Figure 9.6c presents a clearer picture of what seems to be the precursor for rippling and further hierarchical structures. At ~ 8 pulses per spot, the overlapped spots can be identified to be comprised by circular ripples. This was an interesting observation, as so far ripples were observed to be perpendicular to the incident electric field. It was also noted that at the centre of each spot, nano-holes (\( \phi \sim 500 \) nm) were etched into the surface. In the present work, laser-induced nano-bubbles or nano-craters were clearly identified for single and multiple pulses just after amorphisation. These have been explained by Tull et al. [212] as ‘burst bubbles’ rapidly re-solidified after localised vaporisation of melted Si is caused by surface impurities.

It is probable that as the number of pulses is increased, these nano-holes act as ‘light trapping’ sites which then became the ripples and micro-column structures seen at lower scanning speeds (increased number of pulses/spot). It is also suggested that at the edges of the multiple-pulse irradiated spot, ripples realigned running perpendicular to the electric field. Figure 9.6d shows the result of lowering the fluence to 0.09 J/cm\(^2\) whilst still 8 pulses per spot are delivered to the material: rippling vanishes, but nano-holes at the centre of the irradiated spot are still visible. Amorphisation around the crater edges was identified instead of ripples. This indicated a threshold for uniform ripple formation in the experiments which occurred at 0.11 J/cm\(^2\) and above 8 pulses per spot.

### 9.3.5 Single pulse irradiation

Single fs pulses obtained at 100 mm/s were characterised and showed different morphologies than the structures obtained at multiple pulses irradiation. Phase explosion ablation was clearly identified with material ‘splashed out’ towards the edges forming a rim or lip around the crater (fig. 9.7a). This formation mechanism was seen to occur for a wide range of fluence values (\(>3 \) J/cm\(^2\)), with the only difference being a reduction in the spot dimensions. No rippling was observed at this irradiation stage.
From 2 to 0.4 J/cm², a crater was formed with material build-up at its centre (bubble-like structure) and a visible amount of splatter (re-solidified drops of molten material) around its periphery (fig. 9.7b). From SEM images, ripples in the edges could be identified for this fluence range, but followed a concentric orientation around the crater rather than a perpendicular polarization with respect to the incident electric field.

A low-aspect crater in ring formation with material build-up at its centre but virtually no splatter was observed for fluences between 0.2 and 0.3 J/cm². For this morphology, ripples appeared more defined and were found following a concentric pattern but they did not possess the classical perpendicular orientation observed at multiple-pulses irradiation.

An ultra-low spatial profile crater (depth < 5 nm) and with the characteristic white halo of Si amorphisation was distinguished for fluences below 0.19 J/cm². Some amorphised material was also found at the centre of the crater (see fig. 9.7d), but this feature disappeared for lower fluences. No ripple was found at this stage of crater formation.
Figure 9.7 Single pulse irradiation at: (a) 4 J/cm$^2$, (b) 0.5 J/cm$^2$, (c) 0.19 J/cm$^2$, (d) 0.12 J/cm$^2$.

The structural modifications for 750 pulses per spot (0.1 mm/s) were quantified in the graph shown in figure 9.8(a). The effects of a single pulse are also presented in order to distinguish the different surface modification mechanisms behind multiple and single pulse femto-second irradiation (fig. 9.8 b).
Figure 9.8 Relationship between: (a) the size of the laser ablated channel by multiple femto-second pulses and the fluence delivered to the material; (b) spot size by a single femto-second pulse and fluence.

Several points can be drawn from the above observations: multiple passes are needed at low fluences to form ripples. Also for multiple-pulses, it can be said that more intricate forms (i.e. micro-columns, micro-holes with rippled walls and deep micro-channels) are formed from a ‘fingerprint’ given by the interference between incident light and a surface electromagnetic wave (SEW).
On the other hand, single pulses do not form the ‘classical’ LIPSS ripples but rather exhibit different low spatial profiles from amorphisation to ring-rippled craters (see fig. 9.7c-d), to ‘flushed-out’ craters (fig. 9.7a-b).

Below the ablation threshold, a single pulse evokes the characteristic amorphised phase-change of the material (see fig. 9.7d). This feature disappears just below the amorphisation threshold identified in the present work to occur at 0.09 J/cm².

### 9.4 Discussion

The formation of LIPSS on a variety of materials has been much studied over many years since they were identified for the first time by Birnbaum [213]. So far, their formation mechanism is still under meticulous study and it is not the intention of the present work to do an exhaustive investigation on the physics behind it. However, as described in the results section, interesting features were found for multiple and single pulse irradiation which were identified at distinct formation regimes as the laser fluence was taken from a minimum (no material modification whatsoever) to the maximum energy level available.

### 9.4.1 Single pulse femto-second irradiation on Si

Guillermin et al. [214] performed a systematic study on the surface structuring of silicon and copper by static single and multiple femto-second pulses. Although they reported for the first time a different type of ripples for single pulse irradiation, this special feature was presented only in SEM images of zones smaller than the total irradiated. This not only subtracted important information from the total irradiated spot but could have limited the study of a single pulse irradiated near the ablation threshold. Their proposed ripple formation threshold for a single pulse is situated between 0.11 and 0.23 J/cm². These values are very close to the range for
amorphisation and crater with peripheral ripples in ring formation detected in the present work (see fig. 9.8b).

Nevertheless, the ripples they observed were only in the vicinity of the crater’s edges (as shown in figure 9.7c for the structures obtained in the present work) and did not run strictly perpendicular to the electric field polarisation but rather presented a circular or ring arrangement. Taking this into account, in this chapter the following question was raised: Is it possible to produce the classical LIPSS ripples by a single pulse in the femto-second scale?

From the results section it was found that rippling in the single pulse regime occurred only in the periphery of the ablated spot and in a ring pattern. After amorphisation occurred (0.09-0.14 J/cm$^2$) the structure observed from 0.15 to 0.25 J/cm$^2$ (which can be stated as ablation threshold of the material) was characterised by the burst of accumulated material at the centre of the spot with ripples extending towards the edges and no splatter.

Bonse et al. [215] demonstrated that it is possible to form LIPSS on Si by single fs pulses and provided a model to explain this effect. According to the authors, due to a change in the dielectric function of the material after laser excitation, defect-initiated Surface Plasmon Polaritons (SPP) have a rather significant role in the early formation of LIPSS, acting as the seed during the first pulse which precedes an inter-pulse feedback mechanism responsible for ripple generation by multiple pulses.

Taking into account Bonse et al.’s explanation [215] and observations made by other researchers [212, 216, 217], this study confirmed from results that it was possible to form ripples (not necessarily the classical LIPSS perpendicular to $\vec{E}$) after a single pulse. The condition for this material modification was that the trigger pulse was set above a certain threshold (i.e. amorphisation threshold) so that the presence of random defects could contribute to the excitation of the SPP mechanism.

So in order to obtain the classical ripples subsequent pulses are needed after the first pulse for an inter-pulse feedback mechanism to take place, which also promotes ripple realignment with orientation perpendicular to $\vec{E}$. 
Chapter 9-Femtosecond Laser Fabrication of Self-assembled Nanostructured Arrays on Si

9.4.2 Multiple pulse femto-second irradiation on Si

An important observation regarding fs multiple pulse surface modification was that it also occurred for sub-threshold pulses for which there is no apparent surface modification. This phenomenon has been identified as an incubation effect by some authors [210, 217]. Actually, Bonse et al. [210] gave a detailed description and experimental demonstration of the sequence of physical processes behind the interaction of fs pulses and c-Si which included: amorphisation, melting, re-crystallisation, nucleated vaporisation and ablation. They determined that for multiple-pulse irradiation, the difference between the ablation threshold and other physical process e.g. amorphisation (first material modification) becomes uncertain due to morphological changes inside the irradiated spot. So, described as a modification threshold, multiple pulses were found to prompt significantly lower threshold values than single pulses. Rendering incubation as the cause of the decrease in such a threshold, the authors defined the incubation effect as a non ablating modification of the surface related to an accumulation of energy in the material, either by mechanical stress or chemical modification, which prompts defect formation and subsequent local enhancement of the electric field. However, their study could not predict the nature of the incubation effect.

In relation to this incubation effect and following the author’s previous study on the change in wettability by laser-induced amorphisation of Si in the nano-second regime [218], it was observed the same change of wetting behaviour in fs laser processed Si samples at low fluences, below the amorphisation threshold (figure 9.9). Even though this phase-change in the material (or any surface modification whatsoever) was not distinguishable by SEM at fluences below 0.09 J/cm$^2$, the optical micrographs of vapour condensation on fs laser treated regions corroborated that an amorphous phase might have been obtained after a first pulse at 0.12 J/cm (fig 9.9a) and even after 8 pulses per spot below 0.09 J/cm$^2$. This first sub-threshold pulse naturally erodes the first atomic layers of the material [219] and prepares it for the next pulse in an inter-pulse feedback mechanism that promotes the generation of
LIPSS. So it might be possible that the incubation effect detected in Silicon has its roots in a chemical modification of the top atomic layers of the material by the introduction of dangling bonds (defects) characteristic of a-Si.

Figure 9.9 Recognition of fs laser marks after being exposed to warm vapour. The difference in water drops at the micro scale allows the viewer to see by means of an optical microscope: (a) single pulse irradiation at 0.12 J/cm$^2$; (b) channel by multiple-pulse irradiation at 10 mm/s, < 0.09 J/cm$^2$ (all scale bars: 250 µm)
9.5 Conclusion

Single crystalline silicon was processed by femtosecond pulses near the ablation threshold. Different morphologies were obtained for 2 irradiation regimes: single and multi pulse. For single pulse processing, an ablation threshold value of 0.2 J/cm$^2$ resulted in concentric rippling extending towards the periphery of the crater. Multi-pulse irradiation was shown to form the classical LIPSS ripples at sub-threshold pulses, possibly due to an incubation effect. This chapter demonstrated that an amorphised layer produced a change in wettability that might have its roots in the introduction of Si-defects after a single pulse.

The set of various morphologies obtained at different pulse energies, scanning speeds, hatch distance, incident light polarisation resulted not only in ripples but in the generation of nano-holes and micro-columns for which their periodicity allowed for a structural colour effect.

In the next chapter, structural colour properties of such nano-structuring are explored via spectrophotometry. Potential applications not only meet a need in the field of photonics but range from biomedical, tribology, colour marking, microfluidics and photovoltaics.
Astonishingly, laser light interference from fs pulses with a scattering electromagnetic wave (SEW) can readily be used to replicate natural photonic structures that also make use of interference effects to display brilliant colours. Many researchers have successfully produced such nano-patterning in a variety of materials, but not until recently has special attention shifted to the potential application that laser-based, nano-manufacturing processes can offer. In the present work, the optical effect of light modulation by nanostructures oriented perpendicular and parallel to the electric field of the laser beam is investigated. Particular interest is given to the reflected light from the periodic array of such structures, which shows a multi-colour response to white light at different angle views (i.e. iridescence). Moreover, it is studied how higher-order hierarchical structures (i.e. micro-columns) superimposed on the ripples might affect the colour intensity just as it is seen in nature.

Compression/stretching of the spectrum of reflected light is also presented, as well as tuning of the spectrum with a forward/delay shift. These structural colour schemes were possible due to an engineered array of nanostructures which were obtained thanks to a careful selection of laser parameters such as a change in the beam polarization during nano-patterning, different scanning speeds, fluence values, and hatchings. All of these provided an enhanced manipulation of the spectrum of reflected visible light wavelengths which can be successfully done in the same
sample site (small patterned areas), without complex or multiple processing steps, and after just a single scan.

10.1 Introduction

Butterflies are one of the best examples in nature for structural colour. Thanks to the periodicity (in the visible light wavelength) found in the scales of their wings, iridescent colours arise not only because of pigmentation but also due to the interaction of light with such photonic arrangement [167], see fig. 10.1. Currently, there is a strong ongoing research in the field of mimicking such behaviour. Many attempts have been successful in replicating these nano-scale features, but in the end, only the cheapest and simplest methods will prevail and eventually will be transferred to an industrial environment.

![Figure 10.1](image-url)

**Figure 10.1** Nanostructure of butterfly wing scales and corresponding reflectance spectra: (a) *Polyommatus icarus*, (c) *Heliophorus sena* and (d) *Pseudolycaena marsyas*; (b) Transmission electron microscopy image of scale cross-section shown in (a); (e) Transmission electron microscopy image of scale cross-section shown in (d); Reflectance spectra for families (f) Polyammatinae, (g) Lycaeninae and (h) Theclina. [167]
The early stage ripples presented in Chapter 9 possess a very unique optical property: Iridescence, an optical effect for which light is reflected by periodical surface modulations causing destructive interference of some wavelengths and amplification of certain others. Ripples can be regarded as one-dimensional photonic structures, because of their periodicity along one direction: perpendicular to the electric field of incident light. This characteristic in particular can be modified by (changing the polarisation direction of incident laser light) to obtain a shift in the displayed colours at different viewing angles. So, colour modification can not only be obtained from a variation in the observer’s position and/or illumination angle, but from the orientation of the structures and also from the absorption of the nano-structuring which can be intensified by the generation of micro-columns and nano-holes perpendicular to the ripples due to multiple pulses, as it was shown in the previous section. Based on the identified thresholds for ripple formation in this work, nano-structuring of silicon with an effect on structural colour was made possible. In addition, the self-assembled nano-structuring process presented in this chapter does not require multiple-steps to produce single or different colours, as all processing parameters can be controlled in only one scan.

Several technologies have emerged recently as potential contenders for structural colour applications. For instance, important work by Kim et al. [220] included the fabrication of a novel, colour tunable material called ‘M-Ink’. This type of ink was composed by superparamagnetic colloidal nanocrystal clusters (CNCs), a solvation liquid and a photocurable resin. When subjected to an external magnetic field, the CNCs align to form chain-like structures with nano-scale periodicity that can be tuned by the strength of the applied field. This periodicity determines the colour of the diffracted light coming from the ink. In order to fix the structural colour, the ink has to be exposed to spatially-controlled ultraviolet UV light. Moreover, the ‘M-Ink’ requires the inclusion of different processing steps: deposition of thin film containing the CNCs, magnetic field application, UV exposure (these 2 last steps have to be repeated if different colours are to be attained); and finally ‘M-Ink’ washout. For example, the authors required 16 repetitions of colour tuning and UV fixing to produce 16 strips of different colours in an area of 160 µm x 100 µm;
according to their report this could take several seconds which can be categorised as a slow process for an industrial application.

Yang et al. recently showed the colour effects of nano-structuring silicon in 3 different background atmospheres (i.e. air, nitrogen and vacuum) [221]. They reported different colour intensities for each of the structures obtained under different environments, but did not provide an explanation for this. Although their results showed a change in the optical properties of the material, they were confined to only one type of ripple orientation and to a fixed viewing angle which does not offer significant information on the control of the optical properties of the material by femto-second laser structuring.

The present work distinguished a colour intensity effect closely related to the amount of light that is absorbed by higher-order structures on the material. This has a direct effect on the intensity of the colours reflected from the front of the treated samples. Micro-holes and micro-columns (< 1 µm in size) superimposed on the nano-ripples will decrease the reflectivity of the sample as they act as ‘light trappers’. This might also explain the results of Yang et al. [221] regarding the correlation between environment and colourised silicon. From their SEM images, it is noticed that a larger presence of micro-holes provides a darker variation in hue coming from the samples. Samples treated in nitrogen exhibit less presence of such micro-holes and thus more vivid colours.

Dusser et al. [222] applied polarisation dependent, ultra-fast laser processing to 316L stainless steel to develop a structural colour marking technique. Pre-defined colours on the material were obtained by changing the nano-ripple orientation through a half-wave plate. Potentially this technique could have ample applications in laser marking and identification codes, as it offers large quantities of information in small processed areas. Although the study by Dusser et al. [222] was proved to be successful for the intended colorimetric application, no reflectivity results which correlated to the morphology of the laser processed nano-structures were offered.

This study demonstrates how the optical response of the laser nano-fabricated structures can not only be affected by the polarisation of incident light but also by
higher-order structures (i.e. micro-columns superimposed on the nanoripples) and nano-structures (i.e. nano-holes) formed at distinct processing speeds and hatch-scanning distances. These results might suggest that just as in nature a variety of combinations in photonic structures results in a range of vivid colours [223], lasers are indeed an excellent source to mimic natural photonic structures by a self-assembly process.

10.2 Experimental Setup

Having been investigated for many years, laser induced periodic surface structures (LIPSS) can suit this nanofabrication application. The formation of these structures was described in the previous chapter and it is the intention of this chapter to explore the structural colour property of these nano-engineered structures in single-crystalline silicon by a femto-second laser source via spectrophotometry. Back-reflection from the patterned surfaces was measured by a high-resolution fiber optic spectrophotometer (Ocean Optics HR4000CG-UV-NIR) in the wavelength range of 200 to 1100 nm.

![Schematic of reflectivity setup](image)

**Figure 10.2** Schematic of reflectivity setup: (1) Fiber optic reflection probe, (2) spectrophotometer, (3) halogen light source, (4) angular mount, (5) sample holder.
The setup for these measurements is shown in figure 10.2: Light from a halogen lamp (3) is coupled into a (1) reflection probe of 7 optical fibres (6 for illumination around a central one for data collection). The probe is then coupled to the spectrophotometer (2) which is connected to a computer by an USB port. Measurements in scope mode were acquired and displayed with SpectraSuite software. Scope mode refers to raw data signal acquisition by the top sensor in real time. Samples were placed perpendicular to incident light on a sample holder (5), which could be rotated by an angular mount (4) in order to modify the angle of incidence from 0° (normal to the surface) to 90° in increments of 6.4°.

10.3 Results: Reflectivity Measurements

10.3.1 Iridescence

Three effects were distinguished in the samples: iridescence, intensity modulation and colour shift. The first can be appreciated in figure 10.3.

Ripples formed at 0.09 J/cm² by 750 pulses per spot, and a hatch distance of 25 µm oriented perpendicularly to the electric polarization field, were found to present diffraction peaks at different wavelengths in the visible spectrum as the angle of incident light was varied from 0° (normal to the rippled surface) up to 64.3° (fig. 10.3a). When the angle of incidence was varied from 0° up to 20° no diffraction peaks appeared but rather a diminution in the relative intensity of reflected light (> 50%) compared to a bare Si surface.
Figure 10.3 Iridescence spectra for nano-ripples generated at 0.09 J/cm² and scanning speed of 0.1 mm/s (750 pulses per spot) at a hatch distance of 25 µm and perpendicular to \( \vec{E} \) (a) reflected relative intensities at incident angles from 0° to 64.3° (Colours are employed for more clarity and do not necessarily correspond to reflected wavelengths); (b) enlarged view for incident angles from 25.7° to 64.3°; inset: SEM of corresponding ripples (Colours correspond to reflected wavelengths)

Figure 10.4 Digital photographs of nano-rippled Si surfaces (different scanning speeds and hatching, from lower to larger values) taken at different viewing angles when the sample was exposed to natural sunlight (camera: Kodak M340, KODAK AF 3X Optical Aspheric Lens, 35–105 mm (equiv.))
The first diffraction peak occurred at $\lambda = 548$ nm for an incident angle of 25.7°. As mentioned in the experimental setup (section 10.2) a halogen light source was employed as the light source for the relative intensity measurements. This implied that relative contribution of each wavelength interval measured by the spectrophotometer may vary from the colours observed under solar light (see figure 10.4). This is due to the characteristic solar spectral distribution reaching a peak at 500 nm, whilst the halogen lamp presents this peak at ~ 667 nm. This explains the readings presenting a shift towards more yellow and red components, compared to the stronger blue shifts seen under natural sunlight [223].

With increasing angle of incidence, the diffraction peaks shifted towards longer wavelengths (see fig. 10.3b). At 45°, the strongest diffraction peak occurs at ~ 670 nm which corresponds to the peak intensity of the halogen light source. As the incident angle reaches 64.3°, the diffraction peaks flatten.

### 10.3.2 Intensity modulation

Another effect was noted for structuring obtained at a slightly higher fluence (~ 0.12 J/cm²), different scanning speeds and smaller hatch distance: intensity modulation. As it will be shown next, hatch distance has direct influence in the final surface morphology, as very close scanning lines will induce the connection of nano-holes and the formation of bifurcated micro-columns which will decrease the total surface reflectivity.
Figure 10.5 Intensity spectra for nano-ripples generated at 0.12 J/cm², at a hatch distance of 20 µm and scanning speed of: (a) 0.75 mm/s (100 pulses/spot); (b) 1.25 mm/s (60 pulses/spot); (c) 1.5 mm/s (50 pulses/spot); (d) detailed view of (c) for incident angles from 25.7° to 64.3°. (Colours are employed for more clarity and do not necessarily correspond to reflected wavelengths)

In contrast with the spectra shown in figure 10.3 in which intensities for incidence angles from 0° to 12.9° was relatively high compared to the rest of the measurements, the intensity spectra shown in graph (a) from figure 10.5 shows a more uniform intensity modulation for all the incidence angles, and no diffraction peaks.
Figure 10.6 SEM of nano-ripples generated at (a) 0.12 J/cm$^2$ and scanning speed of 0.75 mm/s (100 pulses per spot) at a hatch distance of 20 µm; (b) scanning speed of 1.25 mm/s (60 pulses per spot)

The reason for this can be appreciated in the SEM image of figure 10.6a. A relatively high rate of pulses per spot (~100) and a closed overlap between scanning lines increased the generation of bifurcated micro-columns and nano-holes and reduced the presence of nano-ripples in the surface producing a modulated decrease in reflectivity for all incident angles. As it can be seen, all the spectral intensities are compressed and present a peak at ~ 670 nm, and for incidence angles between 19.3° and 51.4°, the measured intensities are almost identical.

For a lower rate of pulses per spot (< 60), ripples dominated a larger surface area (fig. 10.6 b) and the distinction in diffraction peaks was more apparent (fig. 10.5b) but the colours observed were not as bright because nano-holes still played an important role in decreasing the reflected wavelengths. With 50 pulses per spot, the presence of diffraction peaks (fig. 10.5 c-d) is more differentiable as they appear brighter to the naked eye. However, in order to see the structural colour effect of overlapping nano-ripples, a change in hatch distance was introduced.
Figure 10.7 SEM of nano-rippled surfaces obtained at different hatch distances: (a) 25, (b) 30, (c) 40 µm; and their respective intensity spectra (selected incidence angles per graph are shown for more clarity and colours correspond to reflected wavelengths)

10.3.3 Colour shift due to hatch separation

A larger response in the occurrence of diffraction peaks was observed when the hatch between scanning lines was increased to 25 µm (fig. 10.7 a): The intensity spectra showed a more similar response as the one corresponding to figure 10.3b. But as the hatch distance was changed up to 30 µm (fig. 10.7b), intensity modulation...
accompanied by a shift in the diffracted wavelengths was seen to occur for different incidence angles.

From the spectra in figure 10.7 b, it was seen that the diffraction peaks at 32.1° and 38.6° were higher than for the case of a 25 µm hatch. Also the diffraction peaks at 45° and 51.4° were seen to reduce in intensity. Along with these intensity changes, the reflected wavelengths (i.e. intensity peaks) corresponding to 38.6° - 51.4° red-shifted approximately 20-40 nm. The opposite was seen for an incident angle of 25.7°, at which the shift presented a blue shift of ~ 40 nm. These changes reflected a stretching in the diffraction peaks of the visible light spectrum. In contrast, a compression in diffracted peaks was recorded again for a 40 µm hatch (see fig. 10.7 c), in which the scanning lines and the un-patterned areas are equal. Such a stretching/compression effect in diffracted colours is presented in table 1.

**Table 10.1 Intensity peaks for different hatch distances**

<table>
<thead>
<tr>
<th>Intensity peaks @</th>
<th>25.7°</th>
<th>32.1°</th>
<th>38.6°</th>
<th>45°</th>
<th>51.4°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hatch: 25 µm</td>
<td>590 nm</td>
<td>605 nm</td>
<td>640 nm</td>
<td>670 nm</td>
<td>760 nm</td>
</tr>
<tr>
<td>Hatch: 30 µm</td>
<td>550 nm</td>
<td>605 nm</td>
<td>660 nm</td>
<td>707 nm</td>
<td>780 nm</td>
</tr>
<tr>
<td>Hatch: 40 µm</td>
<td>590 nm</td>
<td>605 nm</td>
<td>650 nm</td>
<td>680 nm</td>
<td>750 nm</td>
</tr>
</tbody>
</table>

Such a kind of shift is better appreciated when the samples are seen under natural sunlight, as the 30 µm hatch sample starts reflecting different colour wavelengths (from purple and blue) at lower incident angles than the 25 µm hatched sample. This implies that if put together and illuminated/viewed from the same angle, consecutive colours (e.g. yellow/green, orange/yellow, red/orange) can be seen at the same time. Also, compressed spectra appear more matte to the observer and stretched spectrums have a more lustrous effect (see figure 10.4 for comparison between matte and bright tones).

The introduction of un-patterned areas can be suggested as the cause for the modulation of intensity, as for all 3 hatches the trend was a general decrease in relative reflectivity. It was noticed that for larger hatch distances, the peaks for all
incident angles became closer and their intensity kept reducing until the effect was lost.

On the other hand, less linking of structures between scanning lines might have been responsible for the stretching shift effect, as for a 30 µm hatch ripples present a more defined morphology and periodicity (~ 660-670 nm) and less light-trapping centres (i.e. nano-holes).

These results indicate that the intensity of iridescent colours can be readily controlled by the introduction of micro-columns and nano-holes that are able to trap light (i.e. by varying the scanning speed), just as the periodic ridges with aperiodic nano-structures found in some butterfly wing scales provide the blackness needed for thermo-regulatory purposes [176, 224]. Also it was seen that a change in ripple coverage, shape and periodicity (which can be influenced by the hatch distance) can have an effect in the colours reflected (i.e. blue-red shift) by a rippled surface at different incident angles.

10.3.4 Colour shift due to ripple orientation

The fourth effect to be seen was that of a colour shift strongly related to the ripples and nano-holes orientation. Figures 10.8-10.10 present examples of ripples that can be obtained by changing the polarisation of incident laser light through a ½ wave plate. Whilst maintaining the same amount of energy delivered to the material, the ripple orientation changed direction as the wave plate was rotated by means of an indexed rotation mount.

The ripple direction was seen to affect directly the colour reflected back from the sample at different viewing angles. The structures superimposed on the ripples and running perpendicular to them are formed due to a higher intensity delivered at the centre of the beam and also contributed to the intensity and distribution of intensity peaks as shown in subsections 10.3.2 and 10.3.3.
The first contrast was observed for ripples oriented 90° and +45° from \( \vec{E} \) (see fig. 10.8 and 10.9). A shift towards shorter wavelengths is seen for the second case. For example, from 25.7° to 45°, the diffracted peaks spectrum covered approximately from ~ 550 nm – 670 nm for ripples oriented +45° from \( \vec{E} \), and from ~590 – 740 nm for ripples perpendicular to \( \vec{E} \).
Figure 10.10 SEM of ripples oriented -45° with respect to $\vec{E}$: (a) hatch: 20 $\mu$m; (b) hatch: 15 $\mu$m.

For ripples at -45° from $\vec{E}$, the spectrum not only shifted towards higher wavelengths but appears more compressed than the last two cases: ~ 600 nm – 670 nm (fig 10.10 a). To verify this, a smaller hatch distance was introduced so nano-holes superimposed on ripples were connected between scanning lines. As it can be seen from fig 10.10b, the spectrum not only remained compressed between 590-670 nm but included incidence angles from 32.1° to 64.3°. Also the peak intensity follows a very unique trend (not previously seen for the 90° and +45° orientations): The peaks decrease uniformly in intensity as the incidence angles are varied from the lowest. Seen under sunlight, these ripples (-45°) give as bright colours as the other orientations; the difference resides in the illumination/viewing angle, which opens the possibility of a wider control of the visible light spectrum by nano-structure orientation.
10.4 Discussion: Structural Colour and its applications

Structural colours are just one example of the magnificence of nature: precisely designed at the nanoscale, they are found in a variety of species (from minerals like opals to plants and animals) with practical purposes such as photoprotection and vision enhancement, signalling, communication, mating, water repellence, thermoregulation, friction and strengthening [166, 169, 225]. It took years of technology development for scientists to realise a way of observing, understanding and finally producing similar structures in many different materials [166, 226-228]. There is no surprise that silicon has been among those preferred by academia and industry, because of its impact in many sectors such as micro-electronics, photovoltaics, photonics, security, biosensors [168].

The photonic bandgap effect observed in these structures is dependent on their periodicity and can be explained by Bragg’s interference law (first mentioned in section 3.3 of chapter 3):

\[ 2\Delta \sin(\theta) = \lambda \quad (10.1) \]

In order to observe a change in the wavelength of reflected light (\( \lambda \)), either the spacing of the nanostructures (\( \Delta \)) or the angle of incidence of electromagnetic radiation (\( \theta \)) has to be modified. Iridescence is the result of altering the latter: as the surface plane is rotated, different colours can be observed, and the outcome is generally a display of vivid and bright colours. In the present work we realised a way of obtaining the same iridescent effect but with the option of modulating the intensity of such a display. The inclusion of light-trapping nano-holes with 2D periodicity was shown to influence the way the spectrum of light behaved in a range of incident angles. More light trapping centres between the ripples compress the reflected spectrum of visible light, giving the displayed colours a matte effect in contrast to the most commonly seen metallic-bright iridescent effect.
The opposite effect takes place if ripples are predominant in the surface (1D periodicity). This stretched spectrum can also be tuned with a forward/delay shift by controlling the occurrence of ripple bands (or hatch separation) and by the orientation of the nanostructures.

All of these effects were obtained thanks to structuring with a periodicity of ~660 – 770 nm. But as the periodicity of these laser-induced structures is also dependent on the wavelength of the laser, this increases even more the possibilities to manipulate and control light just as in nature a myriad of different structures give rise to a wide spectrum of structural colours.

10.5 Conclusion

The set of various morphologies obtained at different pulse energies, scanning speeds, hatch distance, incident light polarisation resulted not only in ripples but in the generation of nano-holes and micro-columns for which their periodicity allowed for a structural colour effect. These nano-structures morphologies were proved to have 3 properties: iridescence, light intensity modulation and colour shifting. The control of these features was possible by a change in laser processing parameters, and has potential not only in laser marking, but in the fields of photonics, biomedical engineering, anti-counterfeit technology, colour marking, microfluidics, tribology and photovoltaics.
CHAPTER 11

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

11.1 Conclusions

The diverse nature of the micro/nano laser-generated structures and their application studied in this research work required the inclusion of individual conclusions at the end of every chapter. Nevertheless, in this final part it is necessary and convenient to provide a list of the main outcomes of this project:

*Technological aspects*

- It is possible to attain solar weighted reflectance (SWR) values below 5% on Si surfaces by means of DPSS Nd:YVO$_4$ laser micro-structuring by multiple scanning passes.
- Laser-microstructuring of Si under an Ar environment can offer better ablation efficiency (enhancement factor of 1.5).
- Amorphous Si nano-bumps of less than 2 nm in height can be generated on single crystal Si by nanosecond pulses at fluence values below the ablation threshold.
- Low-fluence, nanosecond laser irradiation on NiP/Al disks can be employed to fabricate nano and sub-nm elliptical bumps for ultra-low flying heights.
- An extended application of a near-field laser nanofabrication technique based on scanning a focused laser beam over a particle lens array can generate single lines and shapes, in contrast with large area, parallel patterning.
Multi-pulse irradiation of Si by femtosecond laser pulses resulted in the production of ripples. A study of the different irradiation regimes (i.e. single and multiple pulses) was presented, as different hierarchical structures and morphologies can be obtained by varying the number of pulses, fluence, scanning speed and beam polarisation.

Scientific aspects

A strong relationship between surface morphology and topography and the obtained reflectivity values was demonstrated. Deep structures with angled walls offered the best optical performance in terms of enhanced absorption.

Theoretical modelling of the optical performance of Si laser micro-structuring showed good performance in short-circuit simulations, even in the near-infrared for which Si is a weak absorber.

Amorphous Si was shown to exhibit different wetting properties from single-crystal Si. This enabled an ‘invisible marking’ effect on the material which is apparent as a difference in water droplet size when vapour condensates on top of the marks. Such an effect can be observed without complex optical equipment.

It was demonstrated by mathematical modelling of Hertzian classical contact theory that and elliptical shape offers better stiction performance than a circular bump.

Femtosecond nano-structuring of Si resulted in a fascinating structural colour effect. It was demonstrated for the first time that these self-assembled fs structuring has the potential to control light by means of the following properties: iridescence, light intensity modulation and colour shifting (i.e. stretching/compressing, blue-red shift of light in the visible spectrum).
11.2 Recommendations for future work:

(1) Although processing in argon proved to be beneficial to increment the laser micro-texturing efficiency, a current concern is the reduction of the laser-processing time per wafer, as a larger number of passes makes the process slow even if the scanning speed is reasonably fast. Further investigation in this area should be carried out by employing a tighter focus spot and consequently larger fluence values. Also, laser micro-texturing of solar cell surfaces is ready to be tested in real photovoltaic devices to consider its practicality and future commercial implementation.

(2) Laser marking of ‘invisbile’ bumps on silicon showed that it is possible to alter the wetting properties of materials at the nanoscale. This could be successfully implemented in microfluidic devices. Moreover, amorphisation of Si by nanosecond pulses and tighter focus spot sizes can lead to 3D nano-fabrication if KOH etching is utilised after laser scanning. It is worth to investigate different levels of amorphisation by varying the laser fluence, which can result in the realisation of more complex features.

(3) The obtained elliptical nano-bump should be tested in a real-environment to further assess their tribological performance. Moreover, the elliptical contact modelling results could be employed in tribology optimisation of surfaces that are in close proximity and relative motion like MEMs and sliding mechanical contacts, for which stiction and wear are critical factors.

(4) Laser direct scanning of a focused beam over a self-assembled particle lens array of microspheres should be investigated with tighter focusing (in the order of the microsphere size) in order to produce finer micro/nano patterns.

(5) The laser nano-engineered butterfly wing structures obtained in the final part of this project should be explored in other materials like ceramics and metals. Their optical and physical properties should be further investigated in order to realise their full potential in areas like photonics, tribology, bio-engineering, microfluidics and anti-counterfeiting.
REFERENCES


71. Tams, C. and N. Enjalbert. *The Use of UV/Vis/NIR Spectroscopy in the Development of Photovoltaic Cells*. (Courtaboeuf, France; 2009)


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APPENDIX A

Stiction Force model to predict hard disk elliptical LZT performance.

Prepared by Ana Pena and James Wang, September 30th, 2010, Manchester, UK.

ClearAll [Hstart, Hstep, mydata, H, k, Ein, Kin, Cvar, sol1, fmydata]
Hstart=0.5/10^9; (*minimum bump height*)
Hstep=0.1;
RSteps=5000;
mydata=Table[{0,0},{i1,1,RSteps,1}];

Do[
H=Hstart+(i1-1)*Hstep/10^9;
R1=(18/10^6)^2/(8*H); (*Radius of curvature along the major axis of the elliptical bump*)
R2=(9.5/10^6)^2/(8*H); (*Radius of curvature along the major axis of the elliptical bump*)

k=\sqrt{1-\left(\frac{R2}{R1}\right)^{\frac{2}{3}}} ; (*Elliptical modulus*)
Ein=EllipticE[k]; (*Complete Elliptical Integral of the first kind*)
Kin=EllipticK[k]; (*Complete Elliptical Integral of the second kind*)
Cvar=((2 (1-R2/R1))/pi)^{1/3} (((R1 Ein)/R2-Kin) (Kin-Ein))^{-1/6};

u=0.2; (*coefficient of friction*)
W=40/10^3; (*Head load*)
y = \frac{25}{10^3}; \ (*Lubricant’s surface tension*)

A = 0.5/10^9; \ (*Effective Area of the slider*)

d = 2.5/10^9; \ (*Initial film thickness of the lubricant*)

Ni = 0.5 \times 10^{6} / (10 \times 10); \ (*number of asperities under the slider*)

Em = 100 \times 10^9; \ (*Composite Young’s module of elasticity*)

sol1 = NSolve \{(4/3) Ni \times Em \times (H - h)^{3/2} \times ((R1 \times R2)^{1/4} \times Cvar^{-3/2}) == P, \\
(2/y \times h^2) \times (A \times d + Ni \times Pi \times (R1 \times R2)^{1/2} \times h^2) == F, \ u \times (W + F) == S, \ P - W == F\};

S1 = sol1[1][1][2];

P1 = sol1[1][2][2];

F1 = sol1[1][3][2];

h1 = sol1[1][4][2];

mydata[i1][1] = N[H];

mydata[i1][2] = S1, {i1, 1, RSteps, 1}];

(*mydata cannot directly being plotted using List3DPlot, use flatten and then partition*)

(*fmydata = Flatten[mydata]; *)

(*List[Partition[fmydata, 5]]*)

List[mydata]

ListPlot[mydata]

(*End of Program*)
APPENDIX B

Publications produced from work carried out for this PhD are given here in their published format:


Laser generation of elliptical nanometre and sub-nanometre bump arrays on NiP/Al data storage disks and their effect on stiction performance

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2011 Nanotechnology 22 365302

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Laser generation of elliptical nanometre and sub-nanometre bump arrays on NiP/Al data storage disks and their effect on stiction performance

A A Pena¹, Z B Wang¹, J Zhang², N E Wu² and L Li¹

¹ Laser Processing Research Centre, School of Mechanical, Aerospace and Civil Engineering, University of Manchester, Sackville Street, Manchester M60 1QD, UK
² Precision Laser Solutions Pte Ltd, 29 Mandai Estate #03-11, 729932, Singapore

E-mail: Ana.Pena@postgrad.manchester.ac.uk

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Abstract

Elliptical nano-bumps on nickel–phosphorus coated aluminium (NiP/Al) hard disks were fabricated by a laser texturing system (maximum power 8 W, maximum frequency 300 kHz). By carefully selecting the level of laser power attenuation and defocus offset distance, bump height can be controlled below 6 nm and down to the sub-nanometre scale. This type of laser-induced texture (elliptical shape) on a disk surface is expected to provide better control of the stiction force along with the smallest separation distance between the head slider and the disk. Quantitative modelling based on the classical Hertzian theory for elliptic contacts has been carried out with the purpose of predicting the stiction behaviour of the presented elliptical shaped sub-10 nm bumps. It has been found that an elliptical shape not only reduces the overall stiction performance of the laser texturing zone (LZT) compared to the conventional circular shape but also extends the occurrence of the ‘stiction wall’ towards the sub-10 nm regime for ultra-low-glide applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the hard disk drive (HDD) industry, increasing magnetic storage densities require an ultra-low-flying height (below 10 nm) so that the head slider can perform the read/write operation [1, 2]. At storage densities greater than 10 Gb in $^{-2}$, bump heights below 15 nm are necessary [3]. If a 1 Tb in $^{-2}$ aerial density is to be achieved, a head–media spacing (HMS) of 6.5 nm will be required, but this has already been established to go beyond the set of physical limits so far explored [2]. Inherent to the tendency to lower the flying height, is the rise of some tribological issues such as a low glide resonance, less head–disk interference and reduced stiction. To fulfil such requirements, a textured take-off and landing zone placed near the inner diameter of the disk should be carefully designed and generated [4]. Typically, the textures employed for this application are either craters or bumps. Whatever the shape, a smaller cross-sectional area causes fewer perturbations during the slider’s motion. Moreover, it has been identified that this parameter which depends on the bump or crater width has the largest influence on the slider’s operating flying height [5].

Stiction is a critical tribological parameter during HDD operation. It is related to the adhesion tendency between two surfaces that are in close proximity. Therefore in order to overcome surface adhesion, a threshold force value is required. This is known as the stiction force, which in a hard disk must be very low so that the head slider can fly smoothly during take-off and landing operations without damaging the disk and the head. This value strongly depends on the texture characteristics of the landing zone such as bump shape, diameter, height and distribution [6, 7]. Another tribological parameter that must be considered is the wear of the head–disk interface (HDI). This damage occurs due to impacts during the contact start/stop (CSS) process, and surface texture can be adapted to
minimize it [8]. It has also been established that in order to achieve the optimum surface texture that will reduce stiction and HDI wear, there must be a compromise between all the bump characteristics. However, it has to be remembered that the bump height is an imperative factor in the design of the flying conditions of the slider, as this determines the storage density of the magnetic disk.

Hard disk laser texturing at the nanometre scale has been successfully demonstrated by various authors [1, 7, 9–12]. Nevertheless, a particular type of nano-bump with an asymmetric profile has also been generated on a NiP/Al substrate. By scanning the beam along the lateral direction, elliptical bumps consisting of a peak on one side and a valley on the other have been textured on the disk surface. Several studies have acknowledged how this asymmetrical bump having an elliptical contact area shows good wear durability, faster take-off/landing response and lower glide resonance and stiction than the symmetrical circular crater shape [10, 13–17]. All the aforementioned conditions are critical for ultra-low-flying HDIs.

In this paper, we present the outcome of texturing a NiP/Al disk by employing a commercial laser texturing system that delivers excellent repeatability and height accuracy control. To be able to modify the shape, a rectangular mask was introduced in the optical setup. In this way, after a single pulse exposure the bumps attain an elliptical shape that can be tested for low-flying height applications. The fabricated features exhibited an aspect ratio of \( \sim 2:1 \) (18 \( \mu m \) along the major axis, 9.5 \( \mu m \) along the minor axis), and heights as low as 0.5 nm, with extremely high repeatability (\( \pm 0.4 \) nm). In addition, an improved mathematical model to predict nano-bump geometry on stiction characteristics has been employed. This is expected to aid the optimization of the laser nano-texturing process design and parameter selection for hard disk manufacture.

2. Laser processing experimental procedure

Laser irradiation of a NiP/Al disk was carried out with a commercial diode pumped Nd:YAG laser texturing zone (LZT) laser texturing system with the following characteristics: wavelength 1064 nm, pulse duration 82 ns, laser power 8 W and frequency 300 kHz.

This system is able to commercially produce bumps on NiP/Al disks with sub-nanometre accuracy and long term stability. These bumps can achieve 6–8 \( \pm 0.4 \) nm heights, with a circumferential pitch of 16 \( \mu m \) (\( \pm 1 \mu m \)) and radial pitch of 16 \( \mu m \) (\( \pm 1 \mu m \)). This agrees well with the current industrial requirement of a standard deviation of less than 0.4 nm for the bump height and less than 0.2 \( \mu m \) for the bump diameter.

With a beam quality factor (\( M^2 \)) of 1.04 and a beam diameter of 7 mm before focusing the beam onto the target by a single element lens (\( f = 50 \) mm), the calculated focused spot size on the disk is 10 \( \mu m \). In this way, at 0.8 W and 300 kHz the energy per pulse delivered to the disk is 2.67 \( \mu J \) which results in circular bumps having a diameter of the same dimension as the spot size. A 3 mm \( \times 10 \) mm metallic mask was placed before the lens to shape the beam spot from circular to rectangular (see figures 1 and 2 for optical lay-out). A variable attenuator was used to control the laser fluence (pulse energy per spot area) delivered to the substrate.

By adjustment of the laser parameters (i.e. laser power, focal position) and the introduction of the rectangular mask, the structures were modified from 6 nm high elliptical nanobumps (figure 2) to sub-1 nm elliptical nano-bumps (figure 9). The LZT laser system enabled such sub-nanometre patterning...
Figure 2. Laser Precision Solutions Pte LZT system.

on the material with the high precision of a few angstroms (1 Å = 0.1 nm). The bumps exhibited a lateral size of 18 μm along the major axis and 9.5 μm along the minor axis with a periodicity of 17 μm.

Considering that a single pulse per bump was delivered and that the outer diameter (D₀) of the LZT band was set to 4.3 cm, 7505 bumps are to be textured during the first spin.

As the laser operates at a frequency of 18 (10⁻⁶ bumps min⁻¹), the starting spindle speed (ω₀) was set to 2398 rpm. In the same manner, an inner diameter (Dᵢ) of 3.8 cm implied an end spindle speed (ωᵢ) of 2714 rpm for the process.

Regarding the linear scanning speed along the radial direction, the equation for the Archimedean spiral was helpful to define the radial dimension of the textured zone as

\[ R = Rᵢ + \frac{h}{2\pi} \theta \]  

where \( h \) is the step between each revolution and in the present case corresponds to the bump periodicity of 17 μm, \( Rᵢ \) is the inner radius of the spiral, and \( \theta \) is the angular position in radians. By obtaining the first derivative of (1) with respect to time as follows:

\[ \frac{dR}{dr} = \frac{h}{2\pi} \frac{d\theta}{dt} \]  

it is possible to obtain an expression for the linear scanning speed of the process along the radial direction:

\[ v = \frac{h}{2\pi} \omega \].

According to this relationship, the starting linear speed (\( v₀ \)) along the radial direction was 0.679 mm s⁻¹ and the end linear speed (\( v₁ \)) was 0.769 mm s⁻¹. The linear scanning speed along the scanning (tangential) direction was 5.4 m s⁻¹. The production rate for this set of processing parameters is 6.9 s per disk. The processed samples were characterized by a high-resolution (0.1 nm in the z-axis) white light interferometer (Wyko NT1100).

3. Results

After laser texturing, a very distinctive shape was identified by the Wyko optical profiler. It consisted of an elongated elevation in the material in the form of elliptical bumps, as shown in figure 3. These nano-bumps of an elliptical shape provide a minimized contact area without affecting bump density in the landing zone of a hard disk.

A closer examination of a 2D optical profile showed that these bumps present the typical ‘sombrero’ shape across the minor and major axes. This implied a high protrusion in the centre of the bump (height 6 nm ± 0.4 nm, diameter 5 μm), a depression around this protrusion (height < 1 nm) and a smaller rim in the periphery of the bump (height < 1 nm). The overall size of the bump along the minor axis was 9.5 μm (figure 4) and 18 μm along the major axis (figure 5). In both measurements (i.e. major and minor axes) the surrounding depression and rim that accompany the main bump can be noticed in the optical profile image as an intense blue and a white ‘halo’, respectively.

Uniform arrays exhibiting the aforementioned structures were readily obtained, as is shown in figures 6 and 7. Measurements showed a peak-to-peak periodicity of 17 μm across the minor and major axes of the bumps. However, due to the linking of the bumps across their major axis, the ‘sombrero’ shape was lost as the bumps became joined together at their peripheral depression. It is noted that texturing is influenced by the roughness of the substrate (Rₐ: 0.2 nm) and even a small tilt of the plane surface can affect the topographic characteristics of these fine structures.

The original ‘sombrero’ bump with a circular shape (figure 8) is also presented in this paper to show the topographic properties of this feature and how it can be modified into an ellipse in order to provide all the tribological advantages described in section 1. It is also confirmed how these bumps were designed to attain a height of 3.5 nm with a small deviation of only a few angstroms (±0.4 nm). Precision is critical and of great importance in order to fulfill industry demands for low flying height (below 10 nm) in a hard disk application.
Figure 4. Two-dimensional optical profile across the minor axis of an elliptical nano-bump (height 6.3 nm and width 9.4 μm).

Figure 5. Two-dimensional optical profile across the major axis of an elliptical nano-bump (height of 6.3 nm and width of 18 μm).

Figure 6. Two-dimensional optical profile of the periodicity of the elliptical nano-bumps along the minor axis orientation.

Figure 7. Two-dimensional optical profile of the periodicity of the elliptical nano-bumps along the major axis orientation.

The 2D optical profile of a high ‘sombrero’ bump is presented in figure 9. The bump height was 3.5 nm, whilst the diameter was 10.2 μm; an interesting feature is that the central bump is not accompanied by a surrounding ‘dip’ or depression but by a smaller rim approximately 1 nm high. In the optical profile of the textured zone, the main bump is distinguished as a bright spot, whereas the surrounding rim exhibits a more subtle shade.

To further demonstrate the potential of the laser texturing system, bumps of sub-nanometre dimensions in the vertical scale were fabricated (figure 10). These bumps also followed the ‘sombrero’ profile and elliptical shape of the first bumps.
Figure 8. Three-dimensional optical profile image of an arrangement of ‘sombrero’ nano-bumps of circular shape.

These sub-nanometre bumps also presented the typical surrounding depression of a ‘sombrero’ bump, which in this case is also on the angstrom scale (∼0.5 nm ± 0.4 nm) (see figure 11). The total lateral size of the feature (including the surrounding depression) along the minor axis of the ellipse is 12.4 μm, which is 3 μm larger than the 6 nm high elliptical bump reported earlier. This might be explained by the defocusing offset used during the experiments to attain a lower bump height [18].

The 2D profile of the sub-nanometre bump across its major axis can be seen in figure 12. The lateral dimension of the bump including the surrounding depression was 18 μm (in agreement with the 6 nm elliptical nano-bump mentioned earlier) and its height measured from the original surface was 0.5 nm, which confirms the height measurement made across the minor axis. As can be seen from the two-point profile, the surface of the bump appears to be quite rough, though it still has to be remembered that this is a consequence of the ultra-shallow height of the bumps that is of the same order as the original roughness of the disk (R_a ∼ 0.1–0.2 nm).

The height of the central bump measured from the bottom of the surrounding depression to the top was ∼1 nm (figure 13) and its diameter was 6 μm (along its minor axis). As reported in the literature, if the fluence value is further decreased, this central protuberance will keep reducing its height until an extremely small crater (a few angstroms deep) is formed. In our experiments this last feature was not achieved due to the fact that the bump’s height (which is already small enough) is what determines the purpose of the texturing technique for a low-flying height application. Therefore, a crater without a rim around it was found to be of no use.

Naturally, this leads to the question: how small can the bump height be in order to still offer a competitive tribological performance? In order to assess this issue, a model was prepared to determine the benefits and possible limitations of the nanometre and sub-nanometre elliptical bump arrays fabricated in this work. Driven by an ever-decreasing HDI, modelling results are presented in section 4 and compared to the conventional circular shapes.

4. Discussion

4.1. Nano-ridge formation mechanism

During laser irradiation, energy is absorbed by the material and a melt pool is formed when the melting point of the material is reached. Depending on the energy fluence delivered during the process, different convective fluxes arise inside the melting pool due to surface tension gradients (thermocapillary...
effects). Because of this capillary phenomenon, such fluxes trigger a ‘flush’ movement in the melted material towards cooler areas of higher surface energy and when the cooling period starts and resolidification takes place, a permanent modification of the material becomes apparent in the form of a crater [19, 20]. However, chemocapillary effects [9, 21, 22] also play an important role in the final topography. They take place as surface composition gradients arise by temperature-induced vaporization of some species (e.g. phosphorus and oxygen). Areas of lower surfactant concentration have a higher surface energy, which implies that chemocapillary forces resulting from chemical composition gradients can be large enough to reverse the localized flow due to thermocapillarity. Subsequently a ‘sombrero’ or bump shape can be produced.

The are four main types of bumps that can be identified as a result of decreasing the fluence (energy per area) of a nano-second laser interacting with a NiP/Al disk and the subsequent competition between thermocapillary and chemocapillary effects. They are: a deep crater with a low peripheral rim, a double rim or ‘W’ shaped crater (as the result of the centre of the crater moving upwards), a central dome (or the ‘sombrero’ shape) and a ‘bowl’ like shape (this appears when the central dome has reduced its height until it disappears) [9, 20, 21].

Even though in this present paper there was a modification from a circular bump into an elliptical one, the final topography of the bumps was in accordance with the aforementioned shapes. For example, the ‘sombrero’ shape was clearly recognized in the 6 nm elliptical nano-bump and the sub-nanometre elliptical bump, for which the central dome extended along the major axis of the ellipse forming an elongated feature.

4.2. Stiction force modelling

To further study the effect of the elliptical shape and the reduced height of the bumps, mathematical modelling of the stiction force for elliptical Hertzian contacts was carried out. Liu and Li [13] investigated the stiction performance of tilted bumps (i.e. of asymmetrical shape) by modifying an existing...
Stiction model developed by Gui and Marchon [23] for regular and random textures that included the meniscus effect of a liquid lubricant.

The elliptical bumps introduced in the present paper are not tilted, but because of their constant streamline geometry their contact area can be considered to be elliptical. Therefore, by employing the modified model for elliptical Hertzian contacts adapted by Liu and Li [13], initial stiction performance was analysed and evaluated for elliptical bumps below 10 nm and in the sub-nanometre scale.

Hertz’s classic contact theory has been used to predict the stiction values for symmetrical sombrero or crater bumps in which the radius of curvature of the bumps limits the model to a 1D case [23, 24]. However, an elliptical contact has to be examined as a 2D problem in which there are two different radii of curvature corresponding to the major and minor axis of the ellipse (figure 14). The principal radii of curvature for the main axes of the contact ellipse can be calculated by considering the equation for the radius of a spherical cap:

\[ R_{x,y} = \frac{(H^2 + r^2)}{2H}; \]  

(4)

where \( H \) is the height of the cap and \( r \) is the radius of the base area of the cap. In the case of the nanometre/sub-nanometre elliptical bumps presented in this paper: \( H \ll r \), so the equation reduces to

\[ R_{x,y} = \frac{r^2}{2H}. \]  

(5)

The equations that describe the stiction model for elliptical nano-bumps are presented in the following. First,

\[ S = \mu(W + F_m) \]  

(6)

in which \( S \) is the initial stiction force between the elliptical contact and the head slider (flat surface), \( \mu \) is the coefficient of friction, \( W \) is the head load, and \( F_m \) is the total meniscus force. The latter is the result of a layer of liquid lubricant film between the bump and the slider. The menisci formed around the contact points due to surface tension has an inside pressure that pulls both surfaces together and creates an additional normal force [23, 25]. The meniscus force can be expressed as

\[ F_m = P_m A_m = \frac{2\gamma}{h^2}(Ad_0 + N\pi \sqrt{R_1 R_2 h^3}). \]  

(7)

Here \( P_m \) is the meniscus pressure and \( A_m \) the total area of the meniscus which can be calculated from the volume conservation of the lubricant under the effective area of the slider, \( A \). \( \gamma \) is the surface tension of the lubricant, \( h \) is the elastically deformed bump height at rest, \( d_0 \) is the initial lubricant film thickness and \( N \) is the number of asperities under a slider.

By acknowledging the Hertzian contact theory, the total elastic contact force, \( P \), between multiple elliptical bumps and a flat surface can be computed by

\[ P = \frac{\pi}{4}NE^*(H_r - h)^{3/2}(R_1 R_2)^{1/4}C^{-3/2}; \]  

(8)

In (8), \( E^* \) refers to the composite Young’s modulus of elasticity of the interface, and \( E \) and \( K \) are the complete elliptical integrals of the first and second kind for the eccentricity \( e \) or elliptical modulus \( k \) of the contact ellipse. The definition of the latter parameter is

\[ k = \sqrt{1 - \left(\frac{b}{a}\right)^2}; \]  

(9)

where \( a \) and \( b \) denote the major and minor semi-axes of the elliptical contact area. In view of the following approximation [26, 27]:

\[ \frac{b}{a} \sim \left(\frac{R_1}{R_2}\right)^{2/3}; \]  

(10)

the complete elliptical integral of the first and second kind are defined as [28]:

\[ K(k) = \int_0^{\pi/2} \frac{d\theta}{\sqrt{1 - k^2 \sin^2 \theta}}; \]  

(11)

\[ E(k) = \int_0^{\pi/2} \sqrt{1 - k^2 \sin^2 \theta} d\theta. \]  

(12)

To complete the model, the meniscus force can also be expressed as the difference between the contact force and the head load:

\[ F_m = P - W. \]  

(13)

The listed equations were introduced in Mathematica 7.0 software to obtain a model that will show the stiction behaviour of the elliptical nano-bumps as a function of their height, relative radii of curvature, and periodicity. Model parameters were set as follows: lubricant surface tension of 25 mJ m\(^{-2}\), initial lubricant film thickness of 2.5 nm, effective area of the slider of 0.5 mm\(^2\), composite Young’s modulus of elasticity of 100 GPa, head load of 40 mN and coefficient of friction of 0.2. All these parameters were taken from the literature and have been adjusted for an accurate model.
Figure 15. (a) Stiction force (g) plotted against the height of an elliptical nano-bump of 9 μm along its major axis and 4.5 μm on its minor axis. (b) Enlarged view of (a) for a bump height up to 15 nm.

Figure 16. (a) Stiction force (N) plotted against the height of an elliptical nano-bump for a bump spacing of 17 μm for different eccentricity values (or elliptical modulus k). (b) Predicted stiction for an eccentricity (k) of 0.38. (c) Predicted stiction for an eccentricity (k) of 0.5. (d) Predicted stiction for reduced lubricant thickness of 0.8 nm.

been used by other authors in the stiction modelling of the textured take-off and landing zone of NiP/Al disks [23, 24]. Our results were found to be good in agreement with those obtained by Liu and Li [13].

As can be seen from the modelling graphs in figures 15(a) and (b), an extremely small nano-bump height below 10 nm can result in very high stiction. This is due to the fact that there is a minimum value in order for the bump size to have a significant influence in the performance of the LTZ.

Nevertheless, if the eccentricity (k) of the nano-bumps is varied (figure 16(a)), it can be observed that the initial stiction can be greatly reduced (~50%) for elliptical shapes with a higher aspect ratio (i.e. a/b). It has to be recalled that the eccentricity of a circle is equal to zero, so when the elliptical
aspect ratio of the bumps tends to a minimum and they appear more circular, higher stiction is expected. In figures 16(b) and (c), modelling curves are presented for \( k = 0.38 \) and 0.5 which confirms that a more elliptical geometry implies better stiction results as the bump height is reduced.

The influence of the bump dimensions also has an interesting role especially towards the sub-10 nm range. In figure 16(b), it is seen that a bump with a dimension of 4.5 \( \mu \)m along its major axis is not suitable for a sub-10 nm HDL. But if the major axis dimension is set to be >9 \( \mu \)m, a landing zone covered in these elliptical bumps is more appropriate for this application. However, the ultimate design goal will be to achieve smaller stiction values, which could be attained if the streamline geometry gets more elongated as dictated by \( k \sim 0.50 \). Figure 16(c) shows the predicted results for such bumps, which appear to be more favourable for the present application.

Another factor that could be modified in order to improve the stiction performance of sub-10 nm bumps is the thickness of the lubrication film, which could be taken to a minimum of 0.8 nm as suggested by Gui [2].

From figure 16(d) it can be concluded that reduced texture heights benefit from a thinner lubrication film. For example, if the film thickness is reduced to 0.8 nm an elliptical bump of 18 and 9 \( \mu \)m along its major and minor axis, respectively, can be designed to attain a height of 10 nm in order to achieve an initial stiction force of 1.7g. This value can be contrasted against 3g for the same bump characteristics but with a lubricant thickness of 2.5 nm. Similarly, an elliptical bump having an eccentricity of 0.5 (e.g. 18 and 1 \( \mu \)m along its axis) is able to reach an initial stiction force of 0.6g for a 10 nm high bump. The height can be reduced further to 6 nm and the predicted initial stiction would be 1.7g.

These results indicate that the bump height can have a feasible minimum value if design parameters are carefully modified. According to their experimental results, Liu and Li recommended a 14 nm minimum height for an elliptical bump which could still show acceptable tribological performance: an experimental maximum stiction force of 0.6g (their modelling results showed higher values of 1.2g for the same height). The current modelling results suggest that, a reduced height of 10 nm could also provide an initial stiction of 0.6g if the eccentricity was adapted to 0.50 and the lubricant thickness reduced to 0.8 nm.

By comparing the stiction performance of elliptical sombrero and circular crater shapes [24] it was found that the elliptical nano-bumps represent a more advantageous solution for the stiction performance of low-glide interfaces. This can be appreciated in figure 17, in which the lowest height for a conventional circular crater (8 \( \mu \)m diameter) is 14 nm whilst the lowest height for an elliptical bump (18 and 9 \( \mu \)m, respectively, along its principal axes) is 9 nm.

These results indicate that elliptical bumps are not only adequate for the sub-10 nm ultra-low-flying height demanded by the hard disk industry, but yield to much lower stiction values than the conventional circular shapes even if a lubricant film thickness of 2.5 nm is considered. They also suggest that lower lubricant thickness values (e.g. 0.8 nm) will significantly decrease the initial stiction force (e.g. 2.3g for an 8 nm elliptical bump) and further extend the landing textured zone into the ultra-low-flying height region (<10 nm) (see figure 16(d)).

Undoubtedly, an elliptical geometry is more favourable than a circular one for a LITZ application. However, it is interesting to note that for bump heights below 5 nm the theoretical limit in their stiction performance becomes a design challenge. An imminent ‘stiction wall’ for extremely low heights means that fabricating ultra-low regular bumps, though feasible, might be detrimental for the present application if the design parameters are not fine-tuned. So, the current goal not only requires the fabrication of the lowest bumps (as demonstrated in section 3) but also the design of a precise geometry (i.e. elliptical shape with an eccentricity value towards 1) and to consider other factors that might be influential in the HMS limits, such as disk/head overcoat and lubricant film thicknesses.

5. Conclusion

We have reported a regular array of nano-structures on a NiP/Al disk. Their elliptical shape (in the form of narrow, elongated ridges) is expected to enhance the overall tribological characteristics of the landing zone [15]. The reported nanometre- and sub-nanometre-scale elliptical bumps possess a favourable geometry that could be tested for low-flying performance, including stiction, glide resonance, head–disk interference, take-off/landing response and durability in contact start/stop tests. At a production rate of 6.9 s per disk, another novel feature of this type of bump is that they can be designed to attain sub-nanometre height if required in order to meet industry requirements. The close relationship between stiction and wear performance [3] and the ever-decreasing head–media spacing prompted the stiction modelling in this work based on Hertz’s classic contact theory for elliptical contacts. The obtained results may be used in the tribological
optimization of surfaces that are in close proximity and relative motion (e.g. MEMs, sliding mechanical contacts). The model can also be applied to other kinds of substrates (i.e. glass, metals) and other applications in which stiction and wear are crucial concerns.

Acknowledgment

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References

Direct writing of micro/nano-scale patterns by means of particle lens arrays scanned by a focused diode pumped Nd:YVO$_4$ laser

Ana Pena · Zengbo Wang · David Whitehead · Lin Li

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Abstract A practical approach to a well-known technique of laser micro/nano-patterning by optical near fields is presented. It is based on surface patterning by scanning a Gaussian laser beam through a self-assembled monolayer of silica micro-spheres on a single-crystalline silicon (Si) substrate. So far, the outcome of this kind of near-field patterning has been related to the simultaneous, parallel surface-structuring of large areas either by top hat or Gaussian laser intensity distributions. We attempt to explore the possibility of using the same technique in order to produce single, direct writing of features. This could be of advantage for applications in which only some areas need to be patterned (i.e. local area selective patterning) or single lines are required (e.g. a particular micro/nano-fluidic channel). A diode pumped Nd:YVO$_4$ laser system (wavelength of 532 nm, pulse duration of 8 ns, repetition rate of 30 kHz) with a computer-controlled 3 axis galvanometer beam scanner was employed to write user-defined patterns through the particle lens array on the Si substrate. After laser irradiation, the obtained patterns which are in the micro-scale were composed of sub-micro/micro-holes or bumps. The micro-pattern resolution depends on the dimension of both the micro-sphere’s diameter and the beam’s spot size. The developed technique could potentially be employed to fabricate photonic crystal structures mimicking nature’s butterfly wings and anti-reflective “moth eye” arrays for photovoltaic cells.

1 Introduction

In recent years an increased interest in replicating natural behaviours (also known as biomimetism) has attracted a lot of research effort [1, 2]. Research on the micro-nano-structure of butterfly wings has shown them as natural photonic crystals. This has established a strong link between the vivid wing colours and the morphology of the wings [3]. Insects use light manipulation as a means to signal between one another but also for thermoregulation and camouflage purposes. The object of such recent interest on natural photonic structures has its roots in the engineered design by which living organisms manipulate and control light to fulfil specific needs [4]. Structure periodicity dictates the way light behaves when encountering a surface (i.e. reflection, absorption and transmission). To be able to control light in the optical spectrum, structuring of materials has to be done within the same scale typically ranging from hundred nanometres to several micrometres. Dimensions of periodicity (1D, 2D or 3D) affect the electromagnetic band gap of the material in the visual wavelength range [5], which could change surface colour or form anti-reflective surfaces. These surfaces are known as “moth eye”, “nipple arrays” or “subwavelength structures (SWS)” [6–11]. In nature they appear in the eyes of some insects helping them to enhance the photon collection of their visual system and to reduce reflection that could attract predators.

Vukusic found recently that nano-structures on the wing scales of some butterflies enhance optical absorption by 90 to 95% resulting in enhanced black colouration [12]. The explanation for such an effect is attributed to the effective medium theory which states that a subtle change in the optical impedance between two mediums will reduce Fresnel reflection. Many micro- and nano-fabrication techniques could fulfil the challenge of fabricating photonic structures
in a diversity of materials [13–24]. In the long term, only the most economic and feasible ones will prevail as the accepted method of fabrication. We attempt to demonstrate how a widely-recognised near-field nano-patterning technique could be used to fabricate custom-defined single-line micro/nano-structures, or to create 2D photonic structures in delimited areas exhibiting distinct shapes (i.e. curves, lines, spiral forms, letters) instead of simultaneously patterning millions of features over large areas as it has been done until now. This novel approach is presented in this paper based on a technique termed by other authors as a “Contact Particle-Lens Array” technique which relies on the near-field enhancement effect by small particles interacting with a laser beam.

2 Theory

In the Contact Particle-Lens Array (CPLA) technique, the particle mask consists of a self-assembled monolayer which offers massive, parallel nano-structuring with a significant improvement in patterning speed under single laser pulse radiation [25–29]. This near-field patterning mechanism was first identified after surface damage appeared during the process of particle removal by dry laser cleaning (DLC) [30, 31]. The technique was further developed by many authors who have studied the near-field effects of small particles on a substrate when subjected to laser irradiation [32–37]. Transparent spherical particles which compose the monolayer are used as a lens array for focussing far-field laser radiation. The near-field lens array produces a strong field enhancement at each particle-sample contact point. Due to the involvement of evanescent waves, the near-field foci can be scaled below the diffraction limit [25, 38] i.e. super-resolution effect. In order to show the basic physics of the near-field focussing effect induced by a small particle, Mie’s theory modelling of the optical near field around a single particle was carried out. Figure 1 shows the modelling results in a cross sectional view of the normalised local intensity field distribution (normalised electric field intensity $|E|^2$ and the real part of the $z$-component of normalised Pointing vector $\text{Re}[S_z]$) underneath a particle (diameter of 4.74 μm, refractive index of 1.45) in air, when subjected to an $x$-polarised plane wave excitation at a wavelength of 532 nm, and pulse duration of 8 ns. By comparing Fig. 1(a) and Fig. 1(b), one can clearly see that the field distribution of $|E|^2$ differs from the $\text{Re}[S_z]$ field distribution. The difference, again, arises due to the presence of the evanescent wave components in the near-field regions. From Fig. 2(a) and (b), it can also be seen that the focus point for such a particle (in air) is at a position $z/a = 1.2$; very close to the particle surface. It can also be seen that the near-field enhancement decays to half its maximum in the range from $z/a = 1.2$ to $z/a \sim 1.455$ which means that a sample must be kept in near-field distance with the particle lens array for
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3 Experimental

The experimental setup is portrayed in Fig. 2(a). The used sample is a p-type single-crystalline Si wafer, <100> orientation, boron doped with resistivity of 1–10 Ω cm. A diode pumped Nd:YVO₄ laser system (Laserval Violino, wavelength of λ = 532 nm, pulse duration of τ = 8 ns, and a repetition rate of 30 kHz) was applied as the light source. A computer-controlled three-axis Galvanometer beam scanning system is attached to the laser system, allowing fabrication of arbitrary patterns on the sample surface.

In the experiments, the samples were first cleaned with acetone and methanol, followed by a de-ionised (DI) water rinse and then dried. A drop coating method was then utilised to deposit a uniform monolayer of silica (SiO₂) micro-spheres onto the sample surfaces. After this a hexagonal array of particles was formed by a self-assembly process where the quality of the monolayer depends on many factors such as the cleanliness of the surface, wettability, temperature and any environmental disturbance. The obtained monolayer mask in our experiments is shown in Fig. 2(c), and was in reasonably good quality over a large surface area. The non-porous SiO₂ micro-spheres (refractive index of ~1.43–1.46, mean diameter of 4.74 µm) utilised in our experiments were initially buffered in DI water with a 9.8 (wt%) solids content.

The prepared samples coated with particles were then processed with a Gaussian laser beam. The laser focus is in an elliptical shape with a spot size of ~50 µm along minor axis and ~80 µm along major axis. The applied laser fluences were set below the ablation threshold of bare Si in the reported experiments. At laser fluences below ~200 mJ/cm², no apparent material modification takes place on a bare surface. However, due to the field enhancement effect given by the particles, ablation took place at the sites where micro-spheres were located, see Fig. 4. In this way, arbitrary patterns of width in the same scale as the beam size are composed of sub-micrometre structures due to the combination of the conventional laser direct microfabrication technique and the CPLA technique. To the best of our knowledge, such a kind of double-scale texturing (i.e. micro-sized patterns made of sub-micron and/or nano-structures) is reported for the first time. Though in the past several authors have detailed the use of focused Gaussian beams in order to produce nano-patterns in a variety of substrates [40–42], it has not been proposed yet how a focused
Fig. 3 Optical micrograph of a micro-spheres monolayer after laser irradiation by a focused Gaussian beam. SiO$_2$ micro-spheres remained in the surface on top of the generated sub-micro/micro-structures which explains the change in reflectivity. Also shown is the site were a micro-sphere was removed leaving a hole behind (shown inside the circle).

beam can be scanned across a monolayer formation in order to obtain single patterns instead of massive, parallel structuring.

In the experiments the pulse repetition rate was set as 30 kHz and the scanning velocities were varied from 1000 to 5 mm/s, which resulted in multiple pulses being delivered to each spot for the lowest velocities. Although most of the particles can be removed after a single-pulse irradiation, it was noticed that for the lowest fluence applied (150 mJ/cm$^2$) some particles remained on top of the sub-micro-structures possibly due to a small tilt in the scanning beam path. This can be seen in Fig. 3 in which a variation in reflectivity is present in the locations where the Gaussian beam was scanned. The rest of the particles that remained in the areas where the laser beam was not scanned, were removed after the process by sweeping a lens cleaning tissue over the surface. The processed samples were characterised by employing an Optical Microscope (OM, Polyvar MET), a Scanning Electron Microscope (SEM, Hitachi S-3400N) and Atomic Force Microscopy (AFM, Veeco Innova Scanning Probe Microscope).

The patterns shown in Fig. 4(a–c) were generated by the above described technique at laser fluences of 150–200 mJ/cm$^2$, scanning velocity of 5 mm/s and laser repetition rate of 30 kHz (this implies a delivery of 300 pulses per spot). The contrast between the laser scanned lines and the bare substrate is given by the scattering effects of the different generated sub-micro/micro-metre structures. The width of the laser-scribed lines at a fluence of 200 mJ/cm$^2$ is $\sim$72 µm and descends to 34 µm at a fluence of 150 mJ/cm$^2$. Further reductions in width are observed in Fig. 4(d) if the scanning velocity is increased to 100 mm/s (15 pulses per spot) which results in a 24 µm line (formed by about 5 sub-

Fig. 4 SEM images of micro-scale lines made of sub-micrometre structures generated after a focused beam was scanned over a 5 µm spheres array: (a) fluence of 200 mJ/cm$^2$, scanning velocity of 5 mm/s, line width of 72 µm; (b) fluence of 170 mJ/cm$^2$, line width of 53 µm; (c) fluence of 150 mJ/cm$^2$, line width of 34 µm; (d) fluence of 150 mJ/cm$^2$, scanning velocity of 100 mm/s, line width of 24 µm; (e) fluence of 150 mJ/cm$^2$, a scanning velocity of 10000 mm/s (1 m/s) results in the individual mark for each pulse per spot; (f) fluence of 150 mJ/cm$^2$ might also generate amorphisation of Si in the periphery of the elliptical beam.
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micro-structures across the minor axis of the beam), this is smaller than the laser spot size of 50 µm × 80 µm. Due to limitations of our current system it has not been possible to decrease the far-field focal spot size so only a single line of particles is irradiated, but work is being undertaken in order to further reduce such a parameter. Shown in Fig. 4(e) is the effect of depositing only one pulse per spot in the monolayer formation, where the elliptical shape of the beam is clearly appreciated.

4 Discussion

The decrease in sub-micro-structure size in the lateral edges of the laser-scribed lines seen in all the SEM images of Fig. 4 occurred due to very low fluences beneath the peripheral micro-spheres irradiated by the Gaussian beam. Such low fluence values also resulted in the amorphisation of Si under the micro-spheres at these particular edges. The characteristic “white” halo structures seen in amorphised Si [43–45] are presented in Fig. 4(f).

The AFM image in Fig. 5(a) clearly shows the different surface morphologies of ablated sub-micro-structures by a focused Gaussian beam. A change in the height profile according to the laser distribution is clearly defined from the outer part towards the central part of the beam, where structures are at their highest because of the accumulation of molten material in the form of a bump reaching ∼250 nm in height. On the contrary, structures formed at the edges of the Gaussian distribution manifest bumps of height ∼10 nm height and craters of depth ∼10 nm.

A more accurate profile dimensional analysis was done for different morphologies and their different profiles are shown in Fig. 5(b–d), where it can be observed that craters, bumps and “sombrero” shapes can be found across the major axis of the elliptical spot. The larger structures (craters with significant debris around them and bumps formed by debris accumulation) were formed when the central part of the beam was scanned over the contact particle lens array. Their formation is clearly related to the near-field enhancement given by the contact particle lens array when irradiated by the laser beam. Considering the laser intensity near-field enhancement under the micro-spheres and the employed nanosecond laser, photo-thermal ablation in the form melt-expulsion/redistribution could be acknowledged as the material removal mechanism in this process [46–48]. Smaller bumps like the one shown in Fig. 6 can be found in the periphery of the ablation spot, the formation mechanism in this case is different and can be explained by a lower intensity enhancement that can cause convective fluxes inside the melt pool due to surface tension (thermo-capillary effect) [49].

Different computer designed patterns could be easily transferred to the samples by utilising the integrated galvo-scanning system. The obtained results are shown in Fig. 7(a–d), where a high contrast in the images is given by the scattering effects of the laser-generated sub-micro/micro-metre structures described above. This pattern-
Fig. 5  (a) Atomic force microscopy image of a micro-scale line formed by sub-micrometre structures and the respective height profile across the width of the line, which shows a variation in structure height according to the laser intensity distribution; (b-d) Different height profiles of some of the structures found along the beam’s intensity distribution.
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5 Conclusion

We have presented an extended application for a near-field laser nano-fabrication technique that combines conventional direct laser micro-processing and a particle-assisted laser nanofabrication technique to generate micro-patterns that are composed of sub-micrometre/micro-structures. This was demonstrated by rapid scanning a focused Nd:YVO₄ laser beam over a self-assembled particle lens array of SiO₂ micro-spheres on top of a Si surface, however more work is being undertaken in order to produce finer micro/nano-patterns. The obtained sub-micrometre patterns have the potential to replicate natural photonic crystals, such as the “moth eye” and “butterfly wing scale” structures.
Fig. 7 (a–b) Laser-scribed patterns made of sub-micrometre structures when a focused laser beam was scanned over a 5 µm SiO₂ monolayer at a fluence of 170 mJ/cm². Patterns are visible due to the scattering effects of the sub-micro/micro-structures.

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Fig. 7 (Continued)

Fig. 8 SEM micrograph of a self-assembled monolayer of SiO₂ micro-spheres and the proposed scanning path of a focused beam in order to fabricate micro/nano-arbitrary patterns by employing the CPLA technique.

References

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Laser generation of nano-bumps below 2 nm height on silicon for debris-free marking/patterning

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Laser generation of nano-bumps below 2 nm height on silicon for debris-free marking/patterning

A Pena, Z B Wang, D J Whitehead, R Lloyd and L Li

Laser Processing Research Centre, School of Mechanical, Aerospace and Civil Engineering, University of Manchester, Sackville Street, Manchester, M60 1QD, UK
E-mail: Ana.Pena@postgrad.manchester.ac.uk

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Abstract

By rapidly scanning a 532 nm diode pumped Nd:YVO₄ laser beam at nano-second pulses below the ablation threshold, a uniform array of nano-bumps of less than 2 nm in height (diameter of around 20 µm) was generated on a p-type ⟨100⟩ Si wafer. This height is two orders of magnitude lower than previously reported values. The array was produced at 30 000 bumps per second. The effect of laser fluence (energy density) and scanning speed on the characteristics of the nano-bumps was investigated and the wettability of the laser nano-textured surfaces was examined. The mechanisms of nano-bump formation are discussed. Also presented are the application of the technique for debris free, invisible marking/texturing of silicon and the recognition of such marks/patterns.

1. Introduction: laser marking on silicon

Laser marking of crystalline silicon is a well-established process with more than 40 years of applications in the semiconductor industry. Marking of electronic components, wafers, integrated circuits and other items made of this widely used material is of importance to the manufacturers because it allows for information identification, serialization, traceability, copyrighting and even for decoration [1].

Laser marking of silicon started with ‘hard marking’ technology which consisted of laser marks of 5–20 µm depth, fairly visible and durable but with a significant amount of debris around them. Such marks became incompatible with the manufacturing process as the demand for smaller devices increased. This required a new technology by which splatter, debris and depth could be diminished to a minimum. ‘Soft marking’ by diode pumped solid state (DPSS) lasers was then introduced (height to width aspect ratio of marks ~0.01), followed by ‘super soft marking’ (depth of marks ~2.6 µm) in which debris generation was entirely eliminated [2]. However, the drive to achieve smaller feature sizes, larger output and reduced costs has pushed the development of new marking techniques towards the nano-scale.

Micro-peak formation on crystalline silicon [3] has been reported as a feasible, novel marking technology. By directing a Nd:YAG laser beam to a programmable LCD mask, a square array pattern is projected onto a silicon surface. Micro-peaks obtained after the laser irradiation exhibit a size of 3.6 × 3.6 µm², a period of 4.5 µm and a height of 0.3 µm. They are claimed to be easily readable under simple lighting due to their depth to width aspect ratio which can be set to 0.15 under the correct laser parameters. The aspect ratio in conventional laser marking is a very important feature because it determines the visibility of each mark given by the contrast between bright and dark parts when subjected to some sort of lighting.

Even smaller laser-fabricated features such as smooth craters on ⟨100⟩ silicon (depth of 35 nm and diameter of 10 µm) have already been demonstrated [4]. Such structures were claimed to be oxide-free after being processed by 8 ns pulses from a Nd:YAG laser (λ = 532 nm) with a fluence of 3 J cm⁻². Such surface modification was attributed to thermal melting and a thermo/chemo-capillary flow. Similar topography changes in the nanometre scale have been obtained in polyimide [5]. Depending on the laser fluence applied, three regimes were identified: holes (depth of 163 nm), humps (height of 17 nm) having a small dip at the top (depth of...
7 nm) and bumps (height of 21 nm). Formation mechanisms of the last two topographies were attributed to amorphization of the material, thermal or non-thermal fragmentation of the polymer chains and plastic deformations due to residual stresses introduced at elevated temperatures.

In this paper, uniform arrays of nano-bumps of less than 2 nm height (diameter of around 20 μm) are demonstrated on a silicon wafer surface. This height value is two orders of magnitude lower than the above reported values for laser marking applications. The effect of laser fluence and scanning speed on the characteristics of the nano-bumps is reported along with the wettability of the laser nano-textured surfaces. The nano-bumps formation mechanism (aspect ratio of 5(10)^−5 and height of 1–2 nm) is investigated.

2. Laser processing experimental procedure

2.1. Laser marking

Pulsed laser irradiation of p-type, single-crystal Si (1 0 0) (boron doped and resistivity of 1–10 Ω cm) was carried out by means of a diode pumped Nd: YVO₄ laser system (Laservall Violino, wavelength of λ = 532 nm, pulse duration of τ = 8 ns and a repetition rate of 30 kHz) with a computer controlled three axis galvanometer beam scanner.

The substrate surface was scanned by a Gaussian laser beam having an elliptical shape. Measurement of the ablation sites using optical microscopy led to the following spot dimensions: 50 μm along the minor axis and 80 μm along the major axis. Fluence values in this paper are based on such measurements.

When controlling the intensity of the Gaussian beam, a low fluence of 0.72 J cm⁻² resulted in uniform structures of only 1 nm in height and ∼20 μm in width. Processing parameters such as power and scanning speed were varied in order to obtain marks that could not be easily detected unless they were exposed to a difference in temperature with water/moisture condensation.

It was found that laser processing at a fluence of 0.72 J cm⁻², a repetition rate of 30 kHz and a scanning speed of 1 m s⁻¹, resulted in very shallow marks only perceptible to the eye after some minutes of being stored in a cold box at 0 °C or when the surface at 21 °C is exposed to warm vapour (e.g. at 36–37 °C). A single pulse per spot was necessary to achieve a nano-bump structure formation.

Considering the aforementioned laser parameters, an area corresponding to 1 cm² was processed by following a linear scanning regime to cover the whole surface with nano-bumps. Hatch distance between scanning lines was adjusted to 25 μm. In this way, a regular square array of the structures was formed. The total processing time for this region was about 4 s. Moreover, arbitrary shapes (such as letters and spirals) made of these nano-bumps were created and seen without the need for any special lighting or lenses.

![Figure 1. White light interferometer (Wyko NT1100) images of silicon sample surface (a) before laser processing and (b) after laser processing (nano-bumps on top). The used laser fluence was 0.72 J cm⁻².](image)
Figure 2. Typical height profiles (Wyko NT1100) of nano-bumps fabricated at laser fluence of 0.72 J cm\(^{-2}\), showing (a) a radius of \(\sim 10.2 \, \mu m\) and height of \(\sim 1\) nm; (b) nano-bumps period of \(\Lambda = 23 \, \mu m\).

Figure 3. White light interferometer (Wyko NT1100) images of (a) a combination of craters and bumps on silicon sample surface after laser processing at a fluence of 0.83 J cm\(^{-2}\); (b) craters formed at a laser fluence of 0.94 J cm\(^{-2}\).

With a subsequent increase in fluence to 0.94 J cm\(^{-2}\), bumps completely vanished from the surface and were replaced solely by craters (figure 3(b)). The height profile of such craters is shown in figures 4(a) and (b).

Figure 4. Typical depth profiles of craters generated on silicon surface at a laser fluence of 0.94 J cm\(^{-2}\), showing (a) radius of \(\sim 10.2 \, \mu m\) and diameter of \(\sim 3.7\) nm; (b) craters period of \(\Lambda = 29 \, \mu m\).

Figure 5 summarizes the dependence of the nano-structure height (negative values indicate structure depth) as a function of laser fluence. A noticeable change in depth (i.e. a few hundred nm) and a larger amount of debris around the craters was observed when the laser fluence was set above 1.5 J cm\(^{-2}\) (this is not shown in figure 5(a)).

Besides laser fluence, the scanning speed is another important system parameter affecting the process. It should be noted that we fixed the repetition rate to 30 kHz and the scanning speed to \(v = 1 \, ms^{-1}\); this corresponds to one pulse per spot. As the scanning speed changes, the number of pulses per spot will change and the final sample surface topography and period of the structures will vary accordingly. Figures 6 and 7 summarize the dependence of structure height and structure period as a function of scanning speed within a range from 0.8 to 3.0 m s\(^{-1}\), at a fixed laser fluence of 0.72 J cm\(^{-2}\) and a fixed repetition rate of 30 kHz. Within this scanning speed range, structuring resulted in a uniform array of nano-bumps with a clearly defined height and period. At a scanning speed of 0.6 m s\(^{-1}\) (3 pulses per spot), the obtained structures became irregular and craters and nano-bumps were mixed and overlapped without clear spacing between individual spots. When the scanning speed was decreased to 0.1 m s\(^{-1}\) (16 pulses per spot), a dotted line of \(\sim 12.05 \, \mu m\) in width and 10 nm in depth was generated. As the scanning speed decreased further, line width and depth kept increasing.

The scanning speed effect was further studied for other laser fluences. Figure 8 shows the dependence of structure (nano-bumps) height as a function of scanning speed at laser fluences of 0.54 and 0.63 J cm\(^{-2}\). It was noticed that for fluence values below 0.72 J cm\(^{-2}\) and scanning speeds from 0.2 to 3.2 m s\(^{-1}\), the surface was either unaffected (structure height of 0 nm) or populated by nano-bumps (structure height <1 nm).

On the other hand, as shown in figure 9, when the fluence was 0.72 J cm\(^{-2}\) and the scanning speed was less than 0.4 m s\(^{-1}\), craters with depths of a few nanometres (negative-value in
Figure 5. (a) Graph illustrating the change in height profile from nano-bumps to craters as the laser fluence increases from 0.54 to 1.4 J cm$^{-2}$. (b) Wyko image of nano-bump generated at a laser fluence of 0.72 J cm$^{-2}$ and (c) crater generated at a laser fluence of 0.94 J cm$^{-2}$.

Figure 6. Nano-bumps height as a function of scanning speed.

Figure 7. Nano-bumps period as a function of scanning speed.

Figure 8. Variations of nano-bumps height versus scanning speed for laser fluences of 0.54 and 0.63 J cm$^{-2}$.

height) covered the laser-treated surface. The craters only changed to nano-bumps (height of around 1 nm) when the scanning speed increased to 0.8 m s$^{-1}$. However, the crater-to-bump transition trend was not observed for slightly higher fluences of 0.83 and 0.94 J cm$^{-2}$, for which craters do not develop into 1 nm height nano-bumps even if the scanning speed is increased. This observation will be further discussed in section 4.2.

3.2. Scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX) analysis

Different computer designed patterns can be easily transferred to a silicon surface through an integrated galvanometer scanning system. Figure 10 shows SEM images of (a) a spiral pattern and (b) cross grids fabricated on a silicon surface using the following parameters: laser fluence of 0.72 J cm$^{-2}$, scanning speed of 1 m s$^{-1}$ and laser repetition rate of 30 kHz. These laser marks are made of nano-bumps. Clearly a strong contrast can be seen in the SEM image for the processed and non-processed regions. The irradiated areas exhibit the white halo which is typical of an amorphous film [6]. This suggests
Figure 9. Variations of structure height versus scanning speed for laser fluences of 0.72, 0.83 and 0.94 J cm$^{-2}$.

Figure 10. SEM images of laser marks on a crystalline silicon surface made of laser-generated nano-bumps at laser fluence of 0.72 J cm$^{-2}$, scanning speed of 1 m s$^{-1}$ and repetition rate of 30 kHz: (a) spiral pattern, (b) cross grids.

that the material could have gone through a phase transition from single-crystal to amorphous.

SEM images of the craters were also analysed to detect the presence of a possible amorphous layer when the fluence is above the ablation threshold. In figure 11 a white region around the craters is observed; it follows the elliptical shape of the Gaussian beam, exhibits a ‘ring’ feature and is similar to the reported laser amorphized morphologies in the literature [7, 8].

Figure 11. (a), (b) SEM images of a laser-processed silicon sample at a laser fluence of 1.14 J cm$^{-2}$, scanning speed of 2.0 m s$^{-1}$, frequency of 35 kHz and a hatch distance of 0.07 mm.

At a laser fluence of 1.14 J cm$^{-2}$, the craters are only a few nanometres deep and the rim around them is $\sim$0.5 nm high. Because of the Gaussian distribution of the beam, the energy fluence at the centre is sufficiently high to ablate the material. However, the surrounding white annulus could be explained by a phase transition due to lower laser energy delivered to this area. When the laser intensity is decreased, the modified areas are smaller than the nominal laser spot. In our case this results in half the original size along the minor axis of the beam and hence the reduction in the structure diameter.

In order to further investigate the chemical composition of the laser-generated patterns EDX analysis was performed. According to the EDX results (shown in figure 12), no trace of oxygen was found in the samples which excludes oxidation from the process. The white regions in figures 10 and 11 are thus purely silicon in non-single-crystalline states (either amorphous or polycrystalline).

3.3. Surface post-processing: potassium hydroxide (KOH) etch
To further determine the possible phase-change of the laser-processed patterns, we employed a chemical etching method. It has been reported that an amorphous layer on silicon can be used as an etch mask against KOH for micro/nano-fabrication purposes [7, 9, 10]. Based on this, a sample exhibiting an array
Figure 12. EDX spectrum of a laser-generated nano-crater (shown in figure 11(b)). The SUM SPECTRUM is a software tool that calculates the total intensity counts of all the pixels in the image per energy channel.

Figure 13. Wyko images of a laser-treated silicon sample exhibiting a uniform nano-bumps array, generated at (a) a laser fluence of 0.63 J cm\(^{-2}\), 30 kHz, 1 m s\(^{-1}\) and hatch distance of 0.05 mm; (b) same surface after being immersed in a KOH solution at 55 °C for 90 s.

of 1 nm nano-bumps (figure 13(a)) was immersed in a 30 wt% KOH solution at 55 °C for 90 s and under constant stirring. Immediately after this, it was rinsed with abundant deionized water to stop further etching.

The results of this post-processing step are shown in figure 13(b). The laser-generated nano-bumps were not etched, while the non-treated regions were affected by the etchant. Thus, the laser-processed areas masked the material against the typical effects of KOH in silicon which is readily etched in the \(\langle 100 \rangle\) plane [11].

The corresponding height profiles are presented in figure 14. It can be seen that after KOH etching, the nano-bumps height ascends to \(\sim 28\) nm. This means that the etch ratio of the processed region was almost 30 times lower than that of the nano-processed crystalline regions. This etch ratio value agrees well with the result from Kawasegi et al when they etched an amorphous Si layer formed by magnetron sputtering [9]. Although Lam et al [12] have suggested that at low fluences single-crystal Si could undergo a phase change to polycrystalline, this could be excluded in our case due to the fact that the etching rates were similar for crystalline and polycrystalline silicon when they were exposed to 30 wt% KOH [13].

For the laser-generated nano-bumps obtained with a laser fluence of 0.54 J cm\(^{-2}\) (figure 15(a)), which displayed a lower height around 0.8 nm (figure 16(a)), we used a longer etching time (120 s) in order to enhance the etch depth. As can be seen in figure 15(b), the laser-generated nano-bumps remained on the surface and the surrounding non-processed areas were etched much quicker resulting in a bump height of around 27 nm (figure 16(b)). In this case it was possible to distinguish the elliptical shape of the Gaussian beam which was made visible thanks to a longer exposure to the wet etchant. When the etching time was further extended, the nano-bumps started to diminish in height and eventually disappeared from the surface. This indicates that the laser-modified material was entirely removed and could no longer be used as an etch-stop mask.

3.4. Wettability characteristics

The presented nano-structures on Si changed the surface wettability of the material. In our study we observed that vapour condenses into water drops of different sizes depending on the processed and non-processed areas. This vapour condensation effect helps the observer to easily recognize the
Figure 15. Wyko images of a laser-treated silicon sample exhibiting a uniform nano-bumps array, generated at (a) a laser fluence of 0.54 J cm$^{-2}$, repetition rate of 30 kHz, scanning speed of 1 m s$^{-1}$ and hatch distance of 0.04 mm; (b) same surface after being immersed in a KOH solution at 55 °C for 120 s.

Figure 16. Height profile of nano-bumps array at (a) a fluence of 0.54 J cm$^{-2}$ and scanning speed of 1 m s$^{-1}$ (height is ~0.8 nm); (b) same surface after being immersed in a KOH solution at 55 °C for 120 s (height is ~26 nm).

Figure 17. Recognition of laser marks after being exposed to warm vapour. The difference in water drops at the micro-scale allows the viewer to see by means of an optical microscope: (a) a spiral ring, (b) ‘LPRC’ letters.

‘optically invisible’ nano-bumps which otherwise can only be detected by a white light interferometer or an atomic force microscope. Figure 17 shows several examples of such characteristic wetting behaviour. The spiral rings and letters ‘LPRC’ were scribed over the silicon surface. The contour of the letters was patterned with the 1 nm high bumps as previously described. Following their immersion in warm vapour, drops of clearly larger size (13–23 µm) covered the nano-bumps while smaller drops (5–7 µm) dwelled in the unmarked areas. Such difference in drop size is responsible for the change in visibility of the markings. Clearly, the laser marked areas are more hydrophilic thus exhibiting a larger contact line for the liquid and solid interface (lower liquid/solid contact angle). The observed change in the wetting characteristics of laser marked surfaces also depends on the ambient and substrate temperatures because this permits condensation to occur. A larger difference between both temperatures will give a more perceptible ‘invisible marking’ effect.

4. Discussion

4.1. Wetting behaviour before and after laser processing

Crystalline silicon will inherently grow a native oxide layer (1–2 nm high) after polishing, which makes the material more
susceptible to surface contamination [14]. Since surface wettability is influenced mainly by the nature and arrangement of the top surface atomic layers [15], a measured contact angle of $\theta = 58^\circ$ in our non-treated samples is the result of the interaction of water molecules with Si–O bonds on the top surface. This is consistent with the reported values of Dixit et al [16].

Considering that the laser processing was done under air conditions, the observed reduction in contact angle at the micro-scale in the treated samples might have occurred due to the introduction of more Si–OH bonds (silanol groups). This could be explained by a strong interaction of the water molecules in the ambient environment with the dangling bonds from the laser-modified amorphous material.

These silanol groups will make the surface layer more complex because they can permute to form a larger number of different chemical species which will exhibit distinct hydrophilic properties [17]. The chemical behaviour of more silanols created in the surface of the material during the nano-structure generation and possible phase-change transition may clarify the noticeable difference in wettability seen on the marks at the micro-scale.

Laser surface treatment has been used by other authors to modify the wettability and adhesion characteristics of silicon [18]. By employing the fourth harmonic of a Nd: YAG pulsed laser ($\lambda = 266$ nm) to irradiate a silicon sample, they noticed a decrease in contact angle and a change in the surface chemical composition of the material. A laser power of 0.8 to 0.9 W and a scanning speed of 100 $\mu$m s$^{-1}$ led to a decrease in contact angle from $\theta = 47^\circ$ (before laser processing) down to $\theta = 0^\circ$–22$^\circ$ (after laser processing). Energy-dispersive x-ray analysis enabled the authors to determine the relative content of oxygen after laser treatment and x-ray photoelectron spectroscopy (XPS) confirmed the presence of (–OH–) bonds in large proportions compared with other chemical species. Thus, it was suggested that such an oxygen-enriched surface enhanced the hydrophilic behaviour of the samples and hence the improvement of the adhesion forces on the surface. It was also observed that after laser treatment the contact angles were inversely proportional to the surface roughness, which also played a role in the increment of the work of adhesion values. It has to be recalled that such reported contact angle values for the laser-treated and untreated surfaces were measured at the macro-scale by the sessile drop method. These values may vary from the actual contact angles of water drops condensing at the micro-scale on a Si surface, as seen in the wetted laser marks reported in our paper (figure 17).

In this study, the effect of surface roughness on the contact angle measurements is deemed as negligible. This is because in our samples the magnitude of the roughness is too small ($<40$ Å) to affect the wetting behaviour of the laser-treated surfaces. This is in contrast to many of the micro- and nano-structured surfaces studied by other authors [19–25] wherein the roughness is large enough to affect the surface contact angles. An example of how the wettability of a surface can be modified by laser micro- and nano-structuring was demonstrated by Zorba et al [26]. They successfully created a wettability gradient in a crystalline Si surface using a femto-second laser. When the authors varied the fluence, different microstructure morphologies (e.g. micro-ripples and micro-spikes) altered the wetting properties of the material and made it more hydrophobic. At laser fluences above 1 J cm$^{-2}$, they observed that nanometre features covered the micro-features, increasing the overall roughness but contributing in a lesser way to the hydrophobic behaviour of the samples. Although a disordered Si layer (a few nanometres thick) was identified in their laser-processed samples, micro-structuring was considered to be the main mechanism behind the high contact angles obtained.

In our current investigation it is suggested that anisotropic wetting has been made possible due to a modification in the arrangement of atoms in the first layers of the material, apparently when it changes from crystalline to amorphous. It has also been considered that the aspect ratio of the nano-bumps is too low ($5(10)^{-5}$) in order to alter the wetting properties at the surface. Besides helping identify the low-aspect marks, this wetting behaviour could be employed in the preparation of very low-aspect micro-fluidic channels. An example of this is shown in figure 18 wherein it can be appreciated how long water drops tend to elongate and spread along the laser-patterned areas.

4.2. Surface modification

The laser fluences used in this study had very unique effects on the material (i.e. laser-induced amorphization). Acknowledged as interactions below the ablation threshold [27], such effects are noticeable in different ways: surface morphology and microstructure, presence of defects and depletion of components. In the present case, surface morphology (i.e. first signs of nano-bump formation) became an outcome when the amorphization threshold was visibly identified at a laser fluence of 0.5 J cm$^{-2}$. With increased fluence, at 0.72 J cm$^{-2}$ the nano-bumps are at their highest ($\sim$1.2 nm) and it is not until 0.83 J cm$^{-2}$ that the ablation threshold takes place characterized by a decline in nano-bump height ($<0.9$ nm) and the generation of craters accompanied by an outer rim (see figures 1 and 3).
The laser-induced phase transition from the single-crystalline to the amorphous state in Si by a nanosecond laser was first reported by Tsu et al [6]. They produced a thin amorphous layer by employing the fourth harmonic of an Nd:YAG laser (λ = 266 nm, τ = 10 ns). By electron diffraction patterns they noticed that such a layer was characterized by a white colour and had a slight thickness variation above the original surface. The authors concluded that such a phase change occurs when melted Si is rapidly cooled down without an opportunity for material re-crystallization.

The findings from this study suggest that the reported fluence values resulted in a laser-induced phase-change in the material from crystalline to amorphous. Whenever low energies are applied to the substrate by short pulses, heating of a thin surface layer results in a shallow liquid depth, and rapid re-solidification of the material does not allow for epitaxial re-growth [28–31]. This implies that Si atoms cannot rearrange again in an ordered, crystalline form. Instead, a disordered arrangement of Si atoms (some of them having dangling bonds) results in an amorphous layer. Liquid/solid interface velocities must be sufficiently high to promote amorphization from the melt and avoid crystal nucleation with typical values >15 m s⁻¹ for (1 0 0) Si [31–33], which are in agreement with the laser-fluence range used in this study.

Considering this, the nano-bumps are generated when the laser intensity distribution is controlled in such a way that only the central part of the beam is above the material’s amorphization threshold. As the laser intensity increases above the ablation threshold, craters are formed at the centre of the beam while amorphous rims at their edges are created due to the Gaussian-profiled intensity distribution.

5. Conclusion

We have reported the generation of nano-bumps of less than 2 nm height on Si by a diode pumped Nd: YVO₄ laser system at 30 000 bumps per second. The formation of such bumps alters the wettability properties of the substrate. This effect is apparent as a difference in water droplet size when vapour condensation occurs on top of the material. By means of such difference, the laser marks made of such bumps can be visible without the use of complex equipment. This marking technique is debris free, does not introduce contamination of any form to the material and could be implemented straightaway. XPS analysis needs to be done in the future to determine the precise contents (i.e. at levels below one monolayer) regarding all the elements present on the surface samples before and after processing. This will give a better understanding of the wetting and de-wetting processes occurring on the surface of the laser marks. Also the technique could be explored for different applications including micro-fluidics and bioengineering.

References

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