INHIBITION AND ENHANCEMENT OF QUANTIZED,
INTERFERENCE-DRIVEN, ULTRAFast-LASER CLEAVING AND
INTRA-FILM EJECTION WITH ANGLE AND POLARIZATION CONTROL

by

David M. Roper

A thesis submitted in conformity with the requirements
for the degree of Masters of Applied Science
Graduate Department of Electrical and Computer Engineering
University of Toronto

© Copyright 2017 by David M. Roper

Abstract

Inhibition and enhancement of quantized, interference-driven, ultrafast-laser cleaving
and intra-film ejection with angle and polarization control

David M. Roper

Masters of Applied Science

Graduate Department of Electrical and Computer Engineering

University of Toronto

2017

Optical interference and ultra-fast laser interaction within micro-scale transparent films offer a novel means for nonlinear confinement of dissipated energy to facilitate high resolution three-dimensional (3D) nanostructuring. Recently, study of thin-film interference has allowed the formation of thin (≈ 40 nm) nanoscale plasma disks stacked on half wavelength spacing, $\lambda/2n_{\text{film}}$ (film refractive index, n_{film}) in dielectric media. This thesis presents angle and polarization control as methods to manipulate the fringe visibility of $1\ \mu\text{m}$ thick SiO_x thin-films on silicon substrates, also exploring the coherence of film interference effects in tight focusing through modelling of Gaussian beam effects. In doing so, an enhancement or diminishment of the quantized intra-film processing has been definitively demonstrated according to s- and p-polarization states, respectively, opening viable quantized intra-film structuring to previously unsuitable low-contrast thin-film systems. The resulting novel 3D topographies and intra-film stacked micro- and nano-cavity formation represents significant advancement of this field.

Acknowledgements

I have been fortunate enough to have the pleasure to meet and work with so many fantastic people who have directly influenced the work in this thesis. Following this sentiment, these acknowledgements will be awfully long so I suggest readers with limited time skip ahead to the Introduction. They say it takes a village to raise a child, and it definitely takes a research group to complete a Masters degree. I can never fully express how appreciative I am of my mentors within the Herman Group, but I will at least attempt to try.

From Dr. Erden Ertorer I have learnt the importance of balance in an academic life; that things will always work out in the end if you just keep calm, tidy the optical bench and close the laser dust shields. Our discussions over lunch on life, family and academic future have been invaluable.

Directly monitoring my projects, Dr. Stephen “no.” Ho has taught me the importance of questioning the feasibility of my ideas, and fully shaping the concepts behind them before diving in. His wealth of experience in the topics discussed in this thesis have been a resource I have unashamedly accessed frequently. I am incredibly grateful to Dr. Ho for always being available on the end of a phone, and for being non-judgemental when facing trivial questions. Additionally, the cross-sectional imagery presented in Chapter 5 would not have been possible without his expertise in FIB milling - thank you for taking the time to capture these images with me during a busy time of the year.

For training me in laser processing techniques and academic professionalism I am

indebted to Dr. Moez Haque. You have always been there to provide guidance in my project and career choices, and to work through any problems that I had at the University of Toronto. Dr. Haque is responsible for producing the plane wave model discussed in Chapter 3 that forms the understanding on which this thesis is based, and for this I am incredibly grateful.

Dr. Jianzho Li's wealth of knowledge sets the standard for us all to aspire to meet in our careers. Kevin Joseph has always been available to go for a coffee to bounce around a complex problem and lament the frustrations of graduate life. My near-daily lunch trips with Ehsan Alimohammadian have maintained my sanity, and as my cubicle neighbour is the first port of call to discuss any technical problems - I cannot think of anyone more patient. I thank my colleagues for creating a work environment that has allowed me to succeed.

I am nothing but a reflection of the support of my family and close friends, and to them this thesis is dedicated. It would be impossible to list everyone, but to those I do not have space for I hope that I tell you often how appreciative I am of the help that you give. To my parents and role models, Caroline and Richard, your success in the face of adversity and sacrifice has allowed Sam and I to achieve, I will always look to you for guidance. To my brother Sam, your friendship is always cherished and whenever times are difficult, I know I can always rely on the fact that at least I am not as ugly as you. Tipler, your unwavering loyalty has given me a platform to succeed without fear of failure. All those in the Varsity Blues Squash team, you have made my time in Toronto truly special. I thank all my many friends from Cambridge who will always be a source of great knowledge and advice, in particular Dan, Shakti, Matt and Felicity who form the bulk of conversation back home, the latter kindly proof reading this thesis. My best friend Madeleine, I dread to think what would've happened if I had not come to Toronto. I will never take your companionship for granted.

I would like to thank my M.A.Sc. committee members, Prof. Amr Helmy, Prof.

Stewart Aitchison and Prof. Joyce Poon for their helpful suggestions and guidance on the best way to proceed and develop my project.

I cannot finish without acknowledging the mentorship and guidance provided by my supervisor Prof. Peter Herman. The constant drive for me to be better, and a strong emphasis on independence, has improved me greatly as an academic. Thank you for supporting my projects, and taking the risk on bringing me to Toronto to work in your group - in this way you are solely responsible for the life changing experiences, personally and professionally, I have had in Canada.

Lastly, the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Toronto (ECE) are gratefully acknowledged for providing financial support.

Contents

Acknowledgements	iii
Table of Contents	vi
Abbreviations	ix
1 Introduction	1
1.1 Outlook and Motivation	1
1.2 Aims	3
1.3 Chapter-by-Chapter outline	4
2 Background	6
2.1 Femtosecond Laser Processing	6
2.2 Thin-Film Blistering	7
2.3 Laser Modification of Thin-Films	9
2.4 Femtosecond Interferometric Quantized Ejection	11
2.4.1 Thin-Film Interference	11
Fresnel Reflection	11
2.4.2 Quantized Ejection	12
Fluence Control	14
Quantized Blistering	15
2.5 Summary	16

3	Design and Simulation	18
3.1	Coordinate Systems	19
3.2	Controlling Visibility Contrast	20
3.3	Plane Wave Model	21
3.3.1	Material Selection	21
3.3.2	SiO _x -Si: Visibility Variation With Angle	24
3.3.3	Thin-Film Intensity Variation	25
3.4	Finite Difference Time Domain (FDTD)	27
3.5	Experimental Predictions	32
4	Experimental Methods and Setup	33
4.1	Femtosecond Laser System (Amplitude Systèmes)	33
4.2	Beam Delivery and Alignment	34
4.3	Sample Preparation - 1 μm SiO _x on a silicon Substrate	38
4.4	Characterisation of Laser Ablation site Morphology	38
4.4.1	Exposure Patterns	38
4.4.2	Optical Microscopy	39
4.4.3	Scanning Electron Microscopy	40
4.4.4	Focused Ion Beam (FIB) Machining	40
5	Normal Incidence	42
5.1	Results of Normal Incidence Exposure	42
5.2	Discussion of Normal Incidence Exposure	50
6	Angled Incidence	54
6.1	Results of Angled Incidence Exposure	54
6.2	Discussion of Angled Incidence Exposure	63

7	Conclusion	67
7.1	Summary	67
7.2	Future Directions	69
A	Plane Wave Model	70
A.1	Thin-film interference intensity	70
A.2	Visibility variation with angle	82
	Bibliography	95

Abbreviations

The following abbreviations are used in this thesis:

2D Two-Dimensional

3D Three-Dimensional

CCD Charge-Coupled Device

FDTD Finite-Difference Time-Domain

FIB Focus Ion Beam

LIFT Laser Induced Forward Transfer

SEM Scanning Electron Microscopy (/Microscope)

SHG Second Harmonic Generation

TE Transverse Electric

THG Third Harmonic Generation

TM 1. Transverse Magnetic 2. Turning Mirror

UV Ultra-violet

Chapter 1

Introduction

1.1 Outlook and Motivation

Thin-film processing is widely used to tailor function and enhance performance in device applications where micro- and nano-length scales are critical, widely applied in micro-electronics, lab-on-a-chip [3], lab-on-a-foil [4], micro-electromechanical sensors [5], and biosensors [6]. Various physical and chemical means for additive or subtractive modifications are well developed that typically aim for two-dimensional (2D) patterning to create adjustable surface chemistry or topography in films that can localize influence over biological functions [7], optical interactions, electronic phenomena, and mechanical responses. With a preference for top-down patterning, optical lithography or direct laser writing offers flexible interaction controls to structure multiple types of thin to thick film materials.

In the case of transparent films, femtosecond lasers drive non-linear optical interactions that further localize modification into the third dimension. For example, for focusing into the volume of photoresist, multilevel diffractive optic elements have been constructed that, in turn, enabled large volume formation of 3D photonic crystal templates [8, 9]. In non-photosensitive film, the laser interaction can be selectively guided

into a buried interface to drive full film mechanical ejection. This can permit the patterning of conductive coatings on display glass [10] through to new means of biological or electronic printing such as laser-induced forward transfer (LIFT) [11, 12, 13]. At reduced exposure, thin-film delamination enables the formation of interface micro- and nano-channels, and blisters in silica-silicon systems [14, 15], in contrast to the full film ejection produced in LIFT.

Thin-film optical interference has offered a promising means for confining nonlinear interactions, for example, to enable stepwise ablation of organic films [16]. However, directing energetic laser processes to physically structure internally in transparent film has been more challenging. By moving to dielectric materials, Kumar *et al.* introduced a controllable quantized intra-film modification in sub-micron thick Si_3N_4 coated silicon [17, 18]. By confining non-linear interactions to fringe maxima, spaced by $\lambda/2n_{\text{film}}$ through thin-film interference, periodic stacks of plasma disks were formed above critical density that enable a novel intra-film cleaving geometry. Expanding plasma disks in the film can override interface interactions to open nanocavities and lead to blister formation or quantised segment ejection for SiO_x and Si_3N_4 thin films on silicon substrates, for thicknesses in the range of 400 nm [17] to 3.5 μm [2] at multiple laser wavelengths [19].

However, this method is limited to a narrow range of thin-film and substrate combinations, wherein sufficient refractive index contrast is necessary to generate strong interference fringes. Fringe visibility is a key underlying factor that has not been previously examined in facilitating quantized processing of thin films. In particular, enhancing visibility in previously unsuitable material systems is a major objective for improving fabrication controls across more desirable thin-film substrate combinations.

1.2 Aims

This thesis aims to present a flexible solution to the narrow range of currently suitable thin-film and substrate material combinations for interferometric quantized processing. The approach taken relies on harnessing the angular and polarization dependence of the Frensel reflection coefficient at the film-substrate interface, allowing an increase or decrease in the amount of reflection at a boundary between media. In this way, angle and polarization manipulate the light confinement through fringe visibility, thus increasing the processing control through the enhancement (or diminishment) of thin-film visibility. Examining this effect, the transition from full film to quantized intra-film ejection by switching between the p- and s-polarization state, while radiating $1\text{ }\mu\text{m}$ thick SiO_x film on silicon substrates at a high incident angle of 65° , is studied. This SiO_x -Si combination represents an ideal material system for interference study, owing to a moderately high index contrast and widespread relevance to CMOS electronic, Si-photonics, and MEMS applications.

This thesis aims to characterize and study controls over the novel 3D surface topographies formed at normal incidence exposures on thin SiO_x films on silicon substrates. Further, cross-sectional imaging allows the assessment of internal structuring to progress the field of surface and intra-film modification. A comprehensive investigation of the angle and polarization effects over a wide range of incident spot size and fluence exposures is conducted and compared to normal incidence exposures. For the first time, the role of fringe visibility in intra-film and inter-film ejections (i.e. LIFT) has been examined by optical modelling and compared with thin-film ablation morphology to definitively demonstrate the underlying interference control. Further, the influence of Gaussian beam walk-off at high incidence angles are studied. Additionally it is a goal of this thesis to assess the potential production of novel asymmetric feature formation using beam walk effects at high incidence angle, opening a new method of topographical control. The work described in this thesis thereby centres on the production of a refined method of angle-

polarization control in which to tune thin-film fringe visibility and tailor the thickness of ejected segments, representing a basis on which to extend these quantized interferometric ejection phenomena to a broader range of material systems and applications.

1.3 Chapter-by-Chapter outline

This thesis is composed of a range of experimental and theoretical study, with the express goal of meeting the aims laid out in this introduction. Discussion can be divided into the following chapters:

Chapter 2 (Background) reviews background material relevant to the theoretical and experimental work discussed in this thesis. Femtosecond laser processing concepts are discussed, and their application in the modification of thin-film layers is presented. An introduction to the field of thin-film blistering is provided and the primary focus of this thesis is supported by an extensive discussion of the concepts of femtosecond interferometric quantized ejection.

Chapter 3 (Design and Simulation) presents and discusses continuous Plane Wave and Finite Difference Time Domain (FDTD) models that describe the thin-film interference following laser exposure. The process of candidate material selection is provided, with visibility and intensity variation shown for the selected SiO_x -silicon system. Additionally, the influence of Gaussian beam walk off effects on intensity and visibility distributions within the thin-film is discussed, with a threshold film thickness suggested, above which these effects are problematic. At the end of this chapter, several predictions are made which may be fulfilled through the experimentation presented.

Chapter 4 (Experimental Methods and Setup) presents the laser beam delivery and sample alignment, fabrication and characterization methods used for processing thin-films and assessing exposure sites. Here the laser configuration is discussed, and techniques such as optical microscopy, scanning electron microscopy (SEM) and focused

ion beam milling (FIB) are outlined.

Chapter 5 (Normal Incidence) presents the results of normal incidence exposure on 1 μm thick SiO_x films on silicon substrates at a range of fluences. Optical microscopy, SEM and FIB analysis was performed on the exposure sites generated. In this chapter a discussion of the ensuing blisters that are formed takes place, with emphasis on the generation of novel internal structures of stacked micro- and nano-cavities, and fusing of these structures to open large intra-film chambers.

Chapter 6 (Angled Incidence) presents the results of angled incidence exposure on 1 μm thick SiO_x films on silicon substrates, for both the s- and p-polarization states, at a range of fluences and spot sizes. Optical microscopy, SEM and FIB analysis was performed on the exposure sites generated. In this chapter, discussion focuses on understanding the role of visibility in the quantized ejection process, detailing the novel surface topographies generated, with insights presented on the effects of visibility enhancement and diminishment. Here, the effect of polarization state on ejection morphology is presented to confirm a new means of enabling or disabling quantized intra-film ejection.

Chapter 7 (Conclusion) concludes this thesis, with future development directions discussed and key findings summarized.

Chapter 2

Background

2.1 Femtosecond Laser Processing

The formation of micron sized features in undoped polytetrafluoroethylene (PTFE), machined by a 300 fs pulse UV excimer femtosecond laser in 1988 [20], demonstrated for the first time the fabrication potential that has developed more recently into a lucrative global interest in femtosecond laser material processing. In this rapidly expanding research and industrial marketplace, laser processing of a wide range of materials presents the opportunity for single step fabrication and dramatically reduced production times during nano- and micro- scale device manufacturing.

Today we find significant research activity in fabrication of waveguides [21, 22], Bragg gratings [23, 24], couplers [25], filters, active devices and a wide range of other optical sensors [26] with nano-scale resolution. Flexible beam delivery systems offer the opportunity of rapid surface patterning through galvanometer stage design in 2D and 3D configurations [27]. A wide variety of lens configurations provide variable focusing conditions and spot sizes.

Femtosecond lasers are particularly well suited to drive non-linear interactions inside transparent materials, where absorption can be localised to the small focal volumes of a

lens. However, exact material response to an incident pulse is a combination of multiple factors. The numerical aperture (NA) of a focusing lens, laser pulse duration and optical aberrations primarily control the light intensity present in the focal volume that is available for material modification. Careful control of laser parameters can allow mitigation of complimentary damage where, for example, material removal accumulation heating effects are heavily dependent on repetition rate, where laser energy is delivered faster than heat may diffuse [28]. In this case, ablation cooling at extremely high repetition rates can, counter-intuitively, negate heating effects through the removal of material [28]. For single pulse processing, the mechanics of material ejection is also heavily dependant on the physical properties of the target material, where melting temperature, thermal diffusion coefficients and fracture toughness play crucial roles in the processing results, striking the balance between energy dissipation in the material and energy delivery, with variable pulse energies and repetition rates.

In the sections that follow, discussion is focused on background material relevant to the surface modification of thin-films, and in particular the femtosecond laser processing in thin transparent films.

2.2 Thin-Film Blistering

Thin-films exhibiting poor adhesion to their supporting substrates and commonly undergo delamination when prompted by external loading factors [29]. A combination of material properties, interfacial bonding, and energy delivery and release mechanisms play a role in determining the formation of blister surface topographies. The mechanical properties of thin-films, in particular their fracture toughness and Young's modulus, are fair indicators of whether a film can stretch or is likely to fracture before blister formation. Catastrophic film fracture is more likely to be seen in thick brittle films than the observation of stable blistering.

Film deposition, or growth method, has been shown to strongly influence delamination and blister formation, with thermally grown films particularly susceptible to delamination owing to the high compressive stresses that arise during thermal cycles in their growth [30]. A detailed description of the interfacial crack propagation and mixed-mode cracking in stacked film layers is presented by Hutchinson and Suo in [29] and [31].

Intrinsic interface energy, established during deposition or prior laser modification, determines the ease at which a thin-film may be debonded from its substrate and so represents an important controlling factor in blister formation. Different means to drive this separation have been demonstrated. Interface delamination may be driven through thermal strain mismatch [32], tunnel cracking, wrinkling or interface debonding [31, 33]. This is particularly prevalent in thin-film substrate systems where layers differ in mechanical properties dramatically, for example with thin-film metallic coatings on polymer substrates.

Interface delamination can be selectively targeted to enable blister formation where, for example, interfacial fracture can be driven by drawing water into pockets at defects along a thin-film and substrate interface. In water-submerged 13 nm thick polystyrene films on hydrophilic silicon wafers, blisters at heights of 100 nm have been formed through osmotic pressure [34]. Laser processing represents an attractive alternate way to induce blister formation in thin-films, by delivering energy preferentially to a film interface to drive delamination in a controlled interaction. With 0.9 ns laser irradiation, at normal incidence, blistering has been observed to form in SiO_x films (25–100 nm in thickness) grown thermally on Silicon substrates [35, 36]. For thicker 1.2 μm SiO_x films femtosecond pulses have shown a similar response [14]. The interaction of laser pulses with thin-films and substrates represents an flexible way to control inter-film dynamics, and forms the basis of discussion for the sections following.

2.3 Laser Modification of Thin-Films

In the case of transparent film, femtosecond lasers drive non-linear optical interactions that unlock the opportunity to further localize the modification into the third dimension, through interference phenomena driven by reflection at film-substrate interfaces. When focusing into a transparent film, the beam confocal parameter of a laser beam typically exceeds the film thickness by multiple factors. Competing interaction dynamics may be enabled and driven from the substrate and interface, normally confining processing of thin films to top-down structuring or interface interactions. Here, femtosecond lasers present the benefits of thin-film penetration, exhibiting a strong interface interaction preferred to localize at the region of substrate in contact with the film. Non-linear interactions narrow the penetration depth of absorbed light, display non-equilibrium heating of the interface zone, and generate resulting phase explosions and shock fronts leading to dynamic full film ejection or delamination, which may lead to blister formation [26].

Laser induced forward transfer (LIFT), originally described by Bohandy *et al.* [37, 38], is a direct write one step process that makes use of pulsed lasers to separate thin-film materials from a transparent substrate and harness interface interactions. The transfer and point-by-pointing printing from donor to recipient substrates allows the design and tailoring of additional functionality on thin-film devices, and this technique is depicted in Figure 2.1. The process can be used to print novel electronic, biological, and mesoscopic structures [12]. The non-linear physics centred at a film-substrate interface may be employed to, for example, fully eject a film in order to pattern conductive coatings on display glass [10].

Recently, LIFT has found application in biological fields. The development of capacitive biosensors for the detection of DNA hybridization provide fabrication speed and simplicity enhancements over competing methods [39] and transfer of cells in liquid thin-films has been demonstrated with key application in tissue engineering [40] with single cell transfer and isolation possible [41].

Figure 2.1: A cartoon depicting the Laser Induced Forward Transfer (LIFT) process, wherein a segment of a thin-film is transferred from a transparent donor substrate to a target recipient substrate.

Alternatively, top-down laser exposure with an absorbing substrate can be used to change thin-film surface morphology through full film ejection or blister formation. Using weaker laser exposures ($\lambda = 775$ nm, 150 fs) to selectively delaminate 1.2 thick μm SiO_x films on Silicon substrates, McDonald *et al.* demonstrate the formation of femtosecond laser induced delamination to form micro- or nano-channel devices at the film interface [14, 15]. A morphological transition was noted wherein above a fluence threshold of 0.7 ± 0.1 J/cm², the thermal oxide film was observed to be completely removed from the the substrate. At exposures below this threshold the oxide film could be observed to delaminate to form blister-like regions that were demonstrably connectible to form interface channels. Here McDonald *et al.* harnessed the complex interaction dynamics at the thin-film interface, suggesting two factors responsible for observed blister formation: intrinsic stress relaxation within the film, and the interaction between the electron plasma and expanding ablated substrate material due to the femtosecond laser induced breakdown of the material near the Silicon interface.

2.4 Femtosecond Interferometric Quantized Ejection

2.4.1 Thin-Film Interference

Reflection and refraction of light at media boundaries offers control and access to a wide range of optical interaction and effects. Thin-film interference permits the analysis of material properties with techniques such as ellipsometry, where polarization changes on reflection from thin-films can be used to quantify film thickness, and dielectric properties. Fabry-Pérot interferometers, created with thin reflecting surfaces, may be used to precisely measure wavelength and are a crucial tool, for example, in astronomy allowing the selection of emission for single atomic transitions for identifying the make up and expansion of the universe.

Fresnel Reflection

In classical electromagnetic wave theory, a plane of incidence can be defined as the plane made by the propagation direction and the vector perpendicular to the plane of the reflecting (or refracting) surface. Electric field components with vector directions parallel to this plane are donated p-polarized and those perpendicular, s-polarized. In this thesis, polarisation variation was not extended further than pure p- or s-polarised light, but superposition principles are expected to define interactions of mixed states (i.e. circular and elliptical). Reflection and transmission at media boundaries can be described through Fresnel reflection coefficients. These coefficients, R_s (s-polarization: Equation 2.1) and R_p (p-polarization: Equation 2.2) for interfaces are dependent on polarisation, incident angle and the contrast in refractive index of the two media. Here the incident angle at a media boundary, θ_i , and the angle of refraction, θ_t , are related by Snell's law (Equation 2.3) to the refractive index of media either side of the boundary.

$$R_s = |r_s|^2 = \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \quad (2.1)$$

$$R_p = |r_p|^2 = \frac{n_1 \cos \theta_t - n_2 \cos \theta_i}{n_1 \cos \theta_t + n_2 \cos \theta_i} \quad (2.2)$$

$$\frac{\sin \theta_i}{\sin \theta_t} = \frac{n_2}{n_1} \quad (2.3)$$

When entering media of lower refractive index, a critical incidence angle, θ_c , exists such that all light is reflected from this boundary. In the upper limit $\sin \theta_t = 1$, all light is reflected from the boundary in a ‘total internal reflection’ condition for angles θ_i exceeding $\theta_c = \arcsin(n_2/n_1)$. This condition forms the operating principal of optical fibres for telecommunication and endoscopic applications. The centre of interest for experimentation and study in this thesis is dictated by propagation of light from a media of low refractive index, n_{film} , into one of high refractive index, $n_{\text{substrate}}$, at a film-substrate boundary in the condition $n_{\text{film}} < n_{\text{substrate}}$. In this condition a ‘Brewster’s angle’ exists for the p-polarization state such that the Fresnel reflection coefficient, $R_p = 0$, which presents an attractive opportunity for eliminating reflection from an interface. In this way, at the Brewster condition, one can selectively turn off and on interference phenomena through a change in polarization state.

2.4.2 Quantized Ejection

In 2001, interference patterns formed in transparent films showing fringe maxima spaced by Fabry-Pérot interference peaks, $d = \frac{\lambda}{2n_{\text{film}}}$, were initially suggested by Hosokawa *et al.* [16] as an explanation for observed one-shot femtosecond ablated, multi-step ejections in substituted triphenylamine (4,4',4''-tris(3-methylphenylphenylamino)triphenylamine) (m-MTDATA) thin-films on quartz substrates. Producing relatively large features of 100–200 μm in diameter, 500–700 nm in total depth, a laser pulse as short as 150 fs was applied at a fluence of between 200 mJ/cm² and 300 J/cm². The difference between etched steps was noted to match with $d = \frac{\lambda}{2n_{\text{film}}}$. The ablation rate was found to deviate from an analogue response, with etch rates rising in digital units with smoothly increasing fluence. This observation infers a localized deposition of laser energy into thinner periodic zones

in the film. However, it was noted that the dissipation of laser energy “burnt” through the polymer half-wavelength zones to fully dissociate and eject the solid film material. Alternative film materials with higher heat capacity, melt temperature and stiffness may be considered as better candidates to contain a laser dissipated heat zone into a thin, isolated, and stacked layers in the film [17].

A more refined digital etching process and development of fully controllable quantised modification and internal ablative structuring was demonstrated by Kumar *et al.* [17, 18] within dielectric media, Si_3N_4 , in 2014. These ejections were heavily dependent on significantly strong Fresnel reflection at film interfaces to create high contrast optical fringes and thus drive formation of thin nano-plasma disks to open nanocavities within the film or to laser cleave a $\frac{\lambda}{2n_{\text{film}}}$ progression of quantized blister formation and segment ejection.

Figure 2.2: A cartoon (a) showing the division of focal interaction of incident 522 nm laser light into thin interaction zones inside a 500 nm thick Si_3N_4 film. The modulated intensity profile (b) can be calculated for a gaussian-shaped beam together with the electron density profile expected at threshold. Ejected segments observed by SEM, and the formation of intra-film nano-voids (c) can be seen with FIB analysis. [17]

Sub-micron sized sites of digital ejection, segments spaced by $d = \frac{\lambda}{2n_{\text{film}}}$, were observed in 500 nm thick SiN_x films deposited on Silicon substrates, as depicted in Figure 2.2, yielding true micro- and nano-scale feature formation in an transparent film with a single step and single pulse laser process. In the moments after the laser exposure shown in

Figure 2.2a, the time scale of the rapid thermal diffusion on the short fringe-to-fringe spacing would be expected to fall in the picosecond to nanosecond range, $\tau_d = \lambda^2/64n_f^2D$, by considering linear thermal diffusion distances, $\sqrt{4D\tau_d} = \lambda^2/4n_f$, in a film of thermal diffusivity D . With femtosecond pulses driving interactions on timescales magnitudes shorter than thermal diffusion, the formation of thin plasma disks with thickness of 20 to 40 nm occurs at interference maxima according to the non-linear processes outlined by Kumar *et al.* [17], and plotted in Figure 2.2b. The phase-explosion and ablation dynamics have resulted in a novel means for intrafilm processing, where quantized structuring is observed in Figure 2.2c, with the formation of intra-film nano-voids. This phenomena has been demonstrated at multiple wavelengths in Si_3N_4 thin films [19] and extended to 1 and 3.5 μm thick SiO_x films on silicon substrates by Ho *et al.* [2].

Fluence Control

Increasing laser fluence exposure has been demonstrated to reproducibly drive quantized intra-film ejections from sequentially deeper layers of Si_3N_4 [17, 19] and SiO_x [2] on Silicon substrates. For example, work produced by Dr Stephen Ho presented in Figure 2.3 shows scanning electron micrographs (SEM) of single-pulse irradiation spots in 3.5 μm SiO_x film, where terraced ejections of half-wavelength film segments have been opened with a Gaussian beam spot [2]. With a systematic reduction in fluence, the number of ejected segments is seen to decrease in a controlled manner from 6 segment ejection at 99 J/cm^2 (top left) to 3 segment ejection at 3.5 J/cm^2 (bottom right) fluence exposure.

Changing laser fluence offers not only a method of controlling feature depth but also presents a step-terrace micro and nano structure. Through competing interaction dynamics, focusing and increased confinement of ejections from great depths, a reduction in ejected segment diameter is observed with increasing segment number (Figure 2.3).

Figure 2.3: SEM of $3.5 \mu\text{m}$ thick SiO_x film on silicon, irradiated with single femtosecond laser pulses of 515 nm wavelength at decreasing fluence exposures of 99.1 J/cm^2 , 36.3 J/cm^2 , 12.5 J/cm^2 , 6.0 J/cm^2 , and 2.2 J/cm^2 , demonstrating quantized intra-film ejections of 3, 4, 5, and 6 segments respectively [1].

Quantized Blistering

As previously discussed in sections 2.2 and 2.3, laser modification can be used to selectively delaminate thin-film interfaces to form blistering morphology. However, demonstration of intra-film blister formation has proven more difficult. With laser processing phenomena dependent on many competing processes, bandwidth of laser spectrum has also been shown to alter quantized structuring. Shorter bandwidths (and therefore longer pulse durations) allow the formation of interference fringes in thicker films, and gain access to ejection dynamics of more favourable mechanical properties and higher energies. Ho *et al.* observe quantised blister formation [42] when ablating $3.5 \mu\text{m}$ thick SiO_x films on Silicon substrates using short pulse, 45 fs , wide bandwidth ($\Delta\lambda = 30 \text{ nm}$) Spitfire Ti:Sapphire Laser (Spectra Physics Spitfire Pro40) at a wavelength of $\lambda = 800 \text{ nm}$. These structures can be seen in Figure 2.4. After a single layer ejection (evidence left at the edges of the exposure site in Figure 2.4), deeper segments have been shown to form single blister layers. Intra-film blisters on the order of $3 \mu\text{m}$ in diameter have been

observed, raised to heights of $1.3\ \mu\text{m}$ at incident fluence values of $6.3\ \text{J}/\text{cm}^2$ shown in Figure 2.4 (left). At reduced fluence of $5.0\ \text{J}/\text{cm}^2$ smaller cavities have been formed by this technique, enabling the formation of intra-film openings of less than $100\ \text{nm}$ seen in Figure 2.4 (right).

Figure 2.4: Blister formation at fluences of $6.3/\text{Jcm}^2$ (left) $5.0/\text{Jcm}^2$ (right) in $3.5\ \mu\text{m}$ SiO_x films on a Silicon substrate. A pulse duration of 45fs , $\Delta\lambda = 30\ \text{nm}$ with a wavelength of $\lambda = 800\ \text{nm}$ was used. Cross sections are shown with FIB milling and imaged through angled SEM [42].

It is suggested that a short duration, wide bandwidth pulse produced an increased heating effect over each high intensity fringe in the SiO_x thin film, allowing expansion and blister formation ahead of an exploding plasma disk. This contrasts to fracture and ejection observed at longer pulse durations. More studies are required to confirm and further model this morphology. Blister formation in this fashion offers true intra-film modification allowing structures similar to those produced by McDonald *et al.* to be formed within the thin-film [14].

2.5 Summary

In this Chapter, the modification of dielectric thin-films by femtosecond laser interference processing has been introduced and discussed. The central focus of this thesis lies in improving the quantized ejection phenomena introduced in section 2.4, which are controlled

by thin-film interference by reflection at the film-substrate interface. In this way, this thesis proceeds in the study of the influence of irradiation angle and polarization state (modelled in Chapter 3) on quantized ejection in dielectric systems, with the express aim of demonstrating command over the onset of intra-film structuring and full film ejection.

Chapter 3

Design and Simulation

Describing the confinement of light during multi-reflection interference in a thin-film, a visibility coefficient is suggested to connect the formation of interference fringes to the quality and cleavability of quantized ejections. A primary goal of this thesis was understanding the role that fringe visibility and polarization control has on intra-film quantized processing. This requires the development of a reliable way to control visibility, with an understanding the effects of varying incidence angle θ_1 , Fresnel reflection coefficients (Equations 2.1 and 2.2) and refractive index contrast.

In section 3.1, coordinate systems for stage motion and describing optical interference within the thin-film are presented. A brief discussion on the control of fringe visibility through angle and polarization state is included in section 3.2. Outlined in this chapter are the continuous plane wave model, based on Dr. Moez Haque's contribution (section 3.3 and included in Appendix A), and the continuous Finite Difference Time Domain (FDTD) Gaussian beam modelling of light propagation in Thin-films, calculated in Lumerical (section 3.4). Additionally in this section, models for high-angle beam walk-off effects, that may lead to deleterious impact of interference in thick-films, are assessed. The use of these optical models provides the basis for decision making on material selection and experimental design to elucidate polarization control for thin-film quantized

ejection. A discussion of this takes place in section 3.3.1, with analysis of an expected visibility response to angle and polarization state provided in section 3.3.2. With a $1\text{ }\mu\text{m}$ thick SiO_x film on a silicon substrate selected as the appropriate experimental system, these models form a strong basis on which to build a deeper understanding of the quantized ejection process, and form a platform for extending the phenomena to new material systems in the future. A series of predictions and statements are made in section 3.5 as to the implications of thin-film intensity modelled on expected experimental outcomes.

3.1 Coordinate Systems

The geometry of a laser beam incident on a transparent film and substrate is depicted in Figure 3.1. Two sets of axis are labelled: $\mathbf{x}, \mathbf{y}, \mathbf{z}$ representing stage motion with respect to the laser beam, and an $\mathbf{i}-\mathbf{j}$ plane within the thin-film. Here a beam incidence angle, θ_1 , is varied with respect to the sample normal, $\mathbf{j}$. Beam propagation is oriented in the $\mathbf{i}-\mathbf{j}$ plane, with multiple internal reflections, moving in the $\mathbf{i}$ direction, shown by arrows in the film in Figure 3.1.

Figure 3.1: A cartoon showing the orientation of an incident laser beam with respect to the thin-film surface. Stage motion is described by x, y, z axis, and interference of multi-reflection of beams (arrows) is described with respect to the labelled $i-j$ plane. The incident beam is shown to form an angle θ_1 with the j axis in the plane $i-j$.

3.2 Controlling Visibility Contrast

A reliable method was required to control fringe visibility in thin-films for an empirical study. Fringe visibility, expressed in equation 3.1, is calculated by taking the difference between the maximum and minimum values of intensity, and dividing by their sum.

$$Visibility = \frac{ComputedMaximumIntensity - ComputedMinimumIntensity}{ComputedMaximumIntensity + ComputedMinimumIntensity} \quad (3.1)$$

With the intensity distribution inside a film controlled by two factors, attenuation and reflection at media boundaries, visibility can be adjusted by changing Frensel reflection coefficients. These vary with media refractive index, the incident and transmission angles at an interface, and the polarization polarization state of the incident light (s-polarization: Equation 2.1, p-polarization Equation 2.2). By simulating visibility variation with incident angle and polarization, suitable material systems for expression of both quantized

ejection phenomena and the transition to full film ejection can be made, where physical feature formation can be predicted through model analysis. A visibility contrast can also be defined as the difference between two visibility states, either through a polarization change, angle change or both.

3.3 Plane Wave Model

A uniform plane optical wave was simulated entering a thin-film and substrate combination at a variable wavelength, incident angle and polarization. To simplify calculation, 5 forward and 5 backward propagating electric field components (TE and TM) were calculated with angular dependence, and converted to intensity within a modelled thin-film. A rapidly diminishing Fresnel amplitude on multiple reflections meant that 5 round trip calculations were sufficient for accurate modelling. Each field was scaled by appropriate combinations of Fresnel transmission and reflection coefficients determined by the number of corresponding reflections within the thin film. The intensity distribution could then be computed by the modulus square of the total electric field and multiplied by the real component of the thin-film refractive index. Visibility (Figure 3.1) was calculated for 0° to 90° range of incidence angles, for the s- and p-polarization state for a range of thin-film and substrate combinations. The full Matlab script for this model is provided in Appendix A.

3.3.1 Material Selection

A thin-film substrate combination was required to have a suitably large fringe visibility to enable quantized ejection at normal incidence, and that could be tailored above and below a quantized processing threshold through further angle control. Availability of materials was an issue to consider, and though material applications are important, a large visibility range takes preference when selecting suitable candidate combinations in the scope of

this thesis. Few systems have suitably high visibility contrast and material properties for quantized ejection candidacy, where film and substrate combinations require a large refractive index contrast and a stable coating. A thin-film and substrate system was chosen by initially calculating visibilities at normal incidence using the plane wave model (section 3.3). Table 3.1 summarises the candidate systems that were considered promising for quantized processing. Example systems where quantized processing has previously been observed are SiO_x [2] and Si_3N_4 [17], but visibility contrast between s- and p-polarization states at high incidence angles had not previously been simulated.

Table 3.1: Selected trial thin-film and substrate systems with calculated visibility values at normal incidence. The chosen material system is highlighted.

Substrate	Thin-Film	Refractive Index Substrate	Refractive Index Thin-Film	Fringe Visibility
Aluminium	Alumina	$0.86754 + 6.22i$ [43]	1.77[44]	0.997
LiNbO_3	SiO_x	2.3321 [45]	1.46[46]	0.44
silicon	SiO_x	$4.22 + 0.038i$ [47]	1.46 [46]	0.79
silicon	Si_3N_4	$4.22 + 0.038i$ [47]	2.06[48]	0.62

Fringe visibility variation with incidence angle is presented in Figure 3.3.2 for the candidate systems considered. Here the angle tunability of fringe visibility can be assessed and one selects a candidate material system for further study based on contrast achieved through polarization state change at angled incidence. An alumina-aluminium system showed a high predicted visibility of 0.9972 at normal incidence. Whilst the feasibility of surface patterning at normal incidence in this system is clear, the visibility range achievable with angle variation presented in Figure 3.2a is too narrow for a complete study. Additionally, with no prior confirmation of quantized ejection this system would represent a high risk selection, where the oxide-metal interface would present a low threshold for damage. Conversely, a SiO_x thin-film and LiNbO_3 substrate system would provide access to low fringe visibilities, as seen for the p-polarization curve in Figure 3.2b (visibility contrast of 0.06 to 0.57, p- to s-), but presents a poor performance at normal incidence. Si_3N_4 were films first discovered to demonstrate this phenomena [17, 19], but

only show a small visibility contrast in Figure 3.2d. Additionally, Si_3N_4 films fracture easily at higher incident fluences [17], limiting the study of quantized blistering.

Figure 3.2: Visibility calculated for a range of incident angles, θ_1 , between 0° and 80° , and for both s-(blue, dash) and p-(red, dot-dash) polarized light. At $\theta_1 = 0^\circ$ a visibility of 0.79 is found inside the thin film. When incidence angle is increased to $\theta_1 = 65^\circ$, a difference in visibility is seen for s- and p-polarisations, with a transition from 0.85 to 0.16 respectively. The following material systems are presented: a) alumina / aluminium b) SiO_x / LiNbO_3 c) SiO_x / silicon and d) Si_3N_4 / silicon.

A SiO_x film ($n_{\text{film}} = 1.46$ [46]) and silicon substrate ($n_{\text{substrate}} = 4.22 + 0.038i$ [47]) combination expressed a moderately strong visibility contrast of 0.79 at normal incidence and has previously been demonstrated as suitable for enabling quantized phenomena [2]. The comparative plots in Figure 3.2 demonstrate that this system (Figure 3.2c) expresses the greatest enhancement or strong diminishment of visibility of the candidate systems. This system represents the best candidate to demonstrate visibility control with increasing angle of incidence for s- and p-polarized states of light, permitting a systematic study

of the effect of visibility contrast on controlling the intra-film quantized ejection. Additionally, SiO_x represents a more important commercial material, and so is selected for the focus of this thesis.

3.3.2 SiO_x -Si: Visibility Variation With Angle

A more thorough discussion of visibility variation with incidence angle is essential to optimise experimental design and form reliable predictions. Here the dependence of fringe visibility on angle incident at the air- SiO_x interface, θ_1 , for the selected $1\ \mu\text{m}$ SiO_x thin-film on a silicon substrate is reproduced in Figure 3.3 for both s- and p-polarized light. From normal incidence, one notes a widely tunable range of visibility has now opened with enhancement from 0.79 to 0.90 for the s-polarization state (blue-dashed line) with increasing angle of 0 to 90° , whilst visibility is otherwise greatly diminished to a low contrast minima of 0.04 in the limit of 90° for the p-polarization state (red-dashed line).

It is noted that the trend for the p-polarization state does not reach zero. If Brewster's angle, θ_B , were reachable at the film-substrate interface, a reflection coefficient of zero for p-polarized light would result in zero visibility. However, for the SiO_x -Si film-substrate combination, an internal angle, θ_2 , of around $\theta_B = 71^\circ$ would be required to meet the Brewster condition. With a dry air lens, a theoretical maximum angle of $\theta_2 = 43.2^\circ$ can be reached at the SiO_x -Si interface in the limit of incident angle approaching $\theta_1 = 90^\circ$. Hence, Brewster's angle ($\theta_B = 71^\circ$) is not reachable in the film at the SiO_x and silicon interface.

With an incidence angle of $\theta_1 = 65^\circ$ as a practical limit due to available lens working distances, at the maximum achievable visibility contrast, a six fold contrast in visibility from 0.16 for p-polarized light to 0.85 for s-polarized light was predicted (Figure 3.3.2). Here a $10\times$ lens ($\text{NA} = 0.16$) is required, having the added benefit of sufficiently large spot size (radius = $2.3\ \theta\text{m}$) such that no polarization ambiguity is expected at tight

Figure 3.3: Visibility calculated for a range of incident angles, θ_1 , between 0° and 80° , and for both s-(blue, dash) and p-(red, dot-dash) polarized light. At $\theta_1 = 0^\circ$ a visibility of 0.79 is found inside the thin film. When incidence angle is increased to $\theta_1 = 65^\circ$, a difference in visibility is seen for s- and p-polarisations, with a transition from 0.85 to 0.16 respectively. Inset: Experimental beam geometries for normal incidence, left, and angled study, right.

focus. This represents a 5 times reduction or 1.1 times enhancement on the visibility of 0.79 at normal incidence. By using normal and angled beam geometries with s- and p-polarizations (Figure 3.3) this dramatic visibility contrast combined with the fringe-to-interface intensity shifts can be directly compared on the same thin-film system, allowing study of the effect of polarization state and angle ($\theta_1 = 0^\circ, 65^\circ$) on quantized intra-film ejection.

3.3.3 Thin-Film Intensity Variation

The intensity distribution, modelled (section 3.3) for an incident plane wave of 515 nm normalized to an incoming beam intensity of 1, within a $1 \mu\text{m}$ SiO_x thin-film on a silicon substrate at normal incidence is plotted in Figure 3.4. Here negligible dispersion effects are seen in the interference fringes formed. Relative intensities for fringe maxima, fringe minima at the thin-film substrate interface are summarised in Table 3.2. Five full fringes

are revealed within the $1\ \mu\text{m}$ thin-film at vertical displacement, $\mathbf{j}$, as follows: 5th at 88 nm, 4th at 256 nm, 3rd at 432 nm, 2nd at 608 nm and 1st at 784 nm. A partial fringe at 950 nm is referred to as the 0th fringe, where the ejected segment would be considered too thin to survive laser “burn” through, and too easily ejected to be reliably recorded. Hence the thin segment formed due to fringe “0” was normally observed to be removed alongside the 1st segment rather than exhibit its own unique ejection threshold.

At normal incidence, θ_1 , a fringe maximum with intensity $2.3\times$ the incidence intensity is seen in Figure 3.4, that greatly exceeds the observed fringe minima of 0.275. The fringe-to-fringe spacing of 176 nm at normal incidence (Figure 3.4) is increased to 225 nm ($\approx 30\%$ increase) at the selected incident angle of $\theta_1 = 65^\circ$ (Figure 3.5), following the expected fringe spacing $\lambda/2n_{\text{film}}\cos\theta_2$. Interference intensities are shown as marginally lower than fringe minima, where transition to an exponential decay in the silicon substrate occurs for a penetration depth of $\approx 1\ \mu\text{m}$ (not plotted in Figures 3.4 or 3.5).

Figure 3.4: The interference intensity distribution with respect to displacement in the $\mathbf{j}$ direction, in a $1\ \mu\text{m}$ SiO_x film, on a silicon Substrate from a continuous wavelength of 515 nm at normal incidence (normalized to an incident beam of intensity 1).

Figure 3.5: The interference intensity distribution with respect to displacement in the $\mathbf{j}$, in a $1\ \mu\text{m}$ SiO_x film, on a silicon Substrate from a continuous wavelength of 515 nm at an incidence angle of $\theta_1 = 65^\circ$ (normalized to an incident beam of intensity 1).

A difference in Fresnel reflection coefficients (Equations 2.1 and 2.2) at the film-substrate interface for s- and p-polarizations at angled incidence sees a stark contrast in

Table 3.2: A modelled relative intensities for a plane wave, continuous 515 nm Gaussian beam, at fringe maxima and film interface ($\theta_1 = 0^\circ$ and $\theta_1 = 65^\circ$ for the s- and p- polarization states).

	Relative Intensities		
	$\theta_1 = 0^\circ$	$\theta_1 = 65^\circ$, s	$\theta_1 = 65^\circ$, p
Fringe Maxima	2.3	1.803	0.65
Fringe Minima	0.2767	0.1393	0.475
Interface	0.2766	0.1392	0.475

intensity distribution within the film (Figure 3.5). Comparing fringe maxima with the relative SiO_x -Si interface intensities presents opposing predictions of strong interference relative to a weak interface interaction (i.e. maxima to interface ratio $1.805/0.14 = 12.9$) for s-polarization (Table 3.2). Conversely, this intra-film interference is expected to be dominated by strong interface interaction (i.e. maxima to interface ratio $0.65/0.475 = 1.37$) for p-polarization (Table 3.2). Given that laser modification at film-substrates interfaces typically has a lower threshold than inside thin-films (due to stronger substrate absorption), it would appear that for p-polarized light the threshold for full-film ejection is likely to be met before the appearance of any quantized intra-film laser cleaving.

3.4 Finite Difference Time Domain (FDTD)

For a tightly focussed Gaussian beam profile entering a thin film, the interference intensity patterns are further modified by the angle of incidence as sequential beam reflections become offset inside an angled SiO_x film, as shown by the arrows for the inset image in Figure 3.3. With angle, the incident and multiple reflected beams are laterally offset, leading to spatial effects in beam interference intensity. This manifests as a varying visibility contrast when spatial components of different incoming intensities interfere on multiple reflections inside the film.

These spatial effects become increasingly significant as film thickness is increased, such that we might consider a threshold at which this becomes problematic for promoting

Figure 3.6: Schematic showing the a Gaussian beam of beam waist w_0 incident at an angle of θ_1 on a thin-film of thickness h . Here reflection between the a reflected beam from a $w_0/2$ radius meets incident light from the beam centre, at the thin-film surface, to highlight beam walk effects on interference contrast

quantized processing. Whilst this effect varies continuously with film thickness and angle, a suggested threshold condition is the shift of the first reflected beam centre to meet with the incident beam offset by $w_0/2$ radius (i.e. 60% intensity). The geometry of interference between reflected and incident beams at this condition is shown in Figure 3.6. These spatial effects in beam interference intensity are expected to become problematic when the film thickness, h , exceeds the Gaussian beam size, $w_0/2$ ($1/e^2$ intensity radius) according to the factor given by Equation 3.2.

$$h = \frac{w_0 n_2 \sqrt{1 - \frac{n_1^2}{n_2^2} \sin^2 \theta_1}}{4 \cos \theta_1 \sin \theta_1} = \frac{w_0}{1.33} = 1.72 \mu m \quad (3.2)$$

In the presented SiO_x-Si system with a laser beam waist of $w_0/2 = 2.3 \mu m$ and incident angle of $\theta_1 = 65^\circ$, Equation 3.2 limits the maximum film thickness to $h = 1.72 \mu m$, which is comparable to the beam waist value. While below the threshold, a small beam walk-off effect is expected for the $1 \mu m$ film thickness selected in the present study.

To better quantify this walk-off effect, the thin-film interference of the incident 515

nm wavelength Gaussian beam was modelled by FDTD (finite-difference time-domain) simulation (Lumerical Solutions), yielding the intensity patterns as shown in Figure 3.7. The incoming beam was defined by a waist radius of $w_0 = 2.3 \mu\text{m}$ with centre focus position at the top SiO_x surface ($\mathbf{i} = 0 \mu\text{m}$) for an incidence angle of $\theta_1 = 65^\circ$. The resulting intensity distribution in the thin film for identical incoming normalised beams (normalized to an intensity of 1) form an interference pattern in an expected narrow beam waist (i.e. $\Delta \mathbf{i} \approx w_0 / \cos \theta_1$), yielding highly (Figure 3.7a) and lowly (Figure 3.7b) contrasting fringes for s- and p-polarizations, respectively, owing to a higher Fresnel reflection for s-polarization.

FDTD simulations (Figure 3.7) are significant in showing that beam walk-off effects were not deleterious to fringe formation. These simulations yield relative peak intensities of 1.45 for s-polarized light compared with 0.65 for p-polarized light that are only slightly degraded from the case of large beam size ($w_0 \gg h$). However, it is noted that the modelled peak intensity for s-polarized light (1.45) is less than that predicted by the plane wave model in Table 3.2 (1.80) owing to these effects. These values contrast with relative intensities of 0.14 for s-polarized and 0.48 for p-polarized light at the SiO_x -Si interface. Four distinct fringes are therefore predicted with a fringe-to-fringe separation of $\lambda / 2n_{\text{film}} \cos(\theta_2) = 230 \text{ nm}$ (where θ_2 refers to the internal angle).

The beam walk-off effect further leads to a lateral asymmetry of the fringe patterns that manifests as a varying visibility contrast. The fringe visibility was calculated from the intensity profiles of Figures 3.7a and 3.7b to follow along each horizontal fringe and is plotted in Figures 3.7c and 3.7d as function of lateral displacement for s- and p-polarized light, respectively. For the case of the high contrast fringes shown for the s-polarization (Figure 3.7c), all fringes share a strong visibility of 0.86 around the centre interference position ($\mathbf{i} = 2 \mu\text{m}$), matching the calculated value as plotted in Figure 3.3 for an infinite beam size ($w_0 \gg h$). Whereas the peak fringe intensity appears nearly symmetric laterally for each fringe (Figures 3.7a and 3.7b), the intensity minima are significantly lower on

Figure 3.7: FDTD simulations of the intensity distribution for a) s-polarized light and b) p-polarized, in a 1 μm SiO_x thin film on a silicon substrate, for a continuous Gaussian beam of $w_0 = 2.3$ μm waist radius, 515 nm wavelength, $\theta_1 = 65^\circ$ incident angle, and incident beam direction from top left. Interference fringe visibility with lateral displacement in the film, calculated for each fringe (labelled 1 to 4), and combined for c) s-polarized and d) p-polarized light. The $1/e^2$ intensity positions of the interference fringes are indicated by red dotted lines.

the right side of the pattern ($i > 2$ μm in Figure 3.7a), predicting a high asymmetry in visibility as shown especially for the s-polarization case (Figure 3.7c).

Here, increasing visibility is observed when moving from left to right, as reflected rays originating from higher intensity beam positions meet with lower intensity incoming rays, improving the interference contrast to almost 100% for the case of higher positioned fringes (i.e. 1 and 2) as i approaches the beam edge. In contrast, for positions to the left of the beam centre, the weaker reflected rays meet with stronger shifted incident rays, diminishing the visibility contrast. This effect is most dramatic for the top (1st) fringe, with visibility varying from 0.5 to 0.95 at the left and right $1/e^2$ intensity positions, indicated by the red-dashed lines in Figure 2 ($i = -3.75$ μm, $+7.45$ μm). The lowest

Figure 3.8: FDTD simulations of the intensity distribution for normal incidence light, in a $1\text{ }\mu\text{m}$ SiO_x thin film on a silicon substrate, for a continuous Gaussian beam of $w_0 = 2.3\text{ }\mu\text{m}$ waist radius, 515 nm wavelength, $\theta_1 = 65^\circ$ incident angle and incident beam direction from top left. b) Interference fringe visibility with lateral displacement in the film, calculated for each fringe (labelled 0 to 5). The $1/e^2$ intensity positions of the interference fringes are indicated by red dotted lines.

fringe (4th) formed nearest to the SiO_x-Si interface is seen to be least affected by the beam-walk off effect, yielding a nearly symmetric and strong fringe visibility (0.86) with small variance of ± 0.02 across the displacement shown, due to the smallest lateral shift of reflected and incident Gaussian beam interference. A similar trend is observed for the fringe visibility of p-polarized light (Figure 3.7d), however, with a dramatic reduction in both absolute value and gradient, with all fringes sharing a weak visibility of ≈ 0.16 near the fringe centre ($i = 2\text{ }\mu\text{m}$). The formation of narrow cleaving intra-film plasma disks will depend on the visibility values presented here, strongly favouring the s-polarization state for observation of quantized intra-film ejection.

The beam walk off effects modelled here are strictly driven by angled incidence and are not observed at normal incidence. Figure 3.8 shows FDTD simulations completed for normal incidence light at the same material and laser perimeters. In Figure 3.8a, a

peak intensity of 2.3, minima intensity of 0.14 and interface intensity of 0.14 match those values predicted for the plane wave model present in section 3.3. A predicted visibility of 0.79 is shown (Figure 3.8b) to not vary significantly with lateral displacement, as expected without the presence of beam walk-off.

3.5 Experimental Predictions

Considering both the plane wave (section 3.3) and FDTD models (section 3.4) outlined in this Chapter, several predictions or statements can be made as to the effects of angle and polarization on quantized interference phenomena in the selected 1 μm thick SiO_x film on a silicon substrate:

1. Fringe-to-Fringe Spacing: An increase in fringe spacing from an approximate 180 nm to 230 nm should be observed when incidence angle is increased from 0° to 65° .
2. Visibility Contrast between s- and p-polarizations: The transition between quantized and full-film ejection is predicted when switching from the s- to the p-polarization state, at constant fluence.
3. Low Visibility: If no quantized ejection is observed at any fluence, spot size or pulse energy, the fringe visibility must be below a critical visibility such that the interface ejection threshold is reached before intra-film ejection at fringe maxima can occur.
4. Visibility Asymmetry: The beam walk-off effects presented in 3.4 are expected to influence feature appearance, but not be problematic in the formation of interference fringes (with a film thickness of 1 μm being under the suggested 1.7 μm threshold). Given the simulated asymmetric visibility distribution, it is expected that quantized ejection will become asymmetric with increasing incidence angle.

Chapter 4

Experimental Methods and Setup

In this chapter the experimental setup and methods necessary to investigate the interference in, and quantized ejection of, SiO_x thin-films on silicon substrates, and study the influence of angle and polarization control are discussed. In section 4.1 a basic outline of the femtosecond fibre amplified laser system used is presented. In section 4.2 a full discussion of the optical beam delivery and alignment procedure is given. The angle mount used to alter the beam incident angle and control the switching of polarization is also presented in this section. The preparation process of the SiO_x coated silicon samples used in experiments is discussed in section 4.3. Finally, the feature characterization techniques used to classify and analyse laser exposures are described in section 4.4.

4.1 Femtosecond Laser System (Amplitude Systèmes)

Linearly polarized, Gaussian-shaped, 285 fs pulses (measured with an auto-correlator) with $M^2 = 1.14$, and 515 nm wavelength ($\Delta\lambda = 1.4$ nm) were supplied by a fibre-amplified laser system (Amplitude Systèmes, Satsuma) at a repetition rate of 100 kHz. This wavelength was selected based on the simulations discussed in Chapter 3, and this repetition rate was selected based on prior studies [19]. Translational motion under a low-NA focusing lens was achieved to sub-micron precision by 3-axis motion stages (Aerotech

ABL1000) mounted on a granite table.

In previous study of intra-film quantized ejection an IMRA America - μ jewel D-400-VR fibre laser was used to provide femtosecond duration pulses [17], and this is described at length in Dr. Shane Eaton's PhD thesis [49]. The Amplitude Systèmes Satsuma performs a significant proportion of beam control internally, hidden from the operator. Chirped pulse amplification, with pulse stretching followed by amplification and re-compression allows high amplification without fibre damage, and avoids any excess non-linearity - though the user has minimal control over the process. Three wavelengths are available for delivery, IR at 1015 nm or 515 nm and 343 nm achieved with internal second harmonic and third harmonic generation. Software provided by the manufacturer allows some control for an optimization process during initial laser setup. Second and third harmonic crystals can be automatically moved into place when selected, though for the scope of this thesis only SHG was required. Power output is also internally controlled through variation in modulator efficiencies.

4.2 Beam Delivery and Alignment

After selecting the output wavelength, chirped pulse amplification and pulse compression optimization is performed. Exact details of the compression method are unknown, and are regarded a company secret, though optimization is likely performed by movement of a grating or prism. The optimization stage is taken to its maximum, tapered, and then adjusted to maximise 50% modulator efficient power output at the laser head. Reference power readings are taken at 50% and 100% modulator efficiencies for the laboratory records to monitor laser performance over time.

Figure 4.1 shows labelled photos of the optical beam delivery layout directly following the laser head (Figure 4.1 left) to the target (Figure 4.1 right). Mirror TM1a is aligned to capture the SHG output, and can be flipped out of the beam path to unblock mirror TM1b

for the IR wavelength. Apertures A1 and A2 are available to align a beam expander, though this was not used in the present project and is not pictured in Figure 4.1. TM1a is adjusted as light is centred through the closed aperture A1, and this is repeated for TM2 and A2. TM3 moves the beam off of the optical table (Figure 4.1 left), to follow along a vertical granite slab (Figure 4.1 right). Aligning the beam in the direction of the vertical slab, TM3 is adjusted to direct the beam through aperture A3 and the final aperture, A4, is used to align TM4.

With no lens mounted, a glass slide is used at the target position of the x-y stages to reflect light from the translational stage back through the beam path to a now closed aperture A3, and TM5 is adjusted until the reflected and incident beams are collinear. The glass slide can then be placed in the lens mount, which can likewise be tilted to match the reflected and incident beam at A3. Stage Power readings are measured and compared at the lens mount for 50% modulator efficiency, both with and without a lens.

For the experiments at normal incidence in Chapter 5, the fine alignment and positioning of the focus at the sample surface was a relatively straightforward process. The MOD efficiency is reduced to 21% at this point so as to not prematurely ablate the sample during alignment. The laser beam waist at the focus of the lens can be positioned on the sample surface by imaging the reflection leaking through mirror TM5. This transmitted beam was delivered to a CCD camera (∞ conjugate lens - Pixelink Camera). A low-angle tilt stage (Newport TTN80) mounted on the motion stages was used to make small angular corrections for deviations in focus with x and y translation to ensure that the beam was normal to the sample to within a few mRad. This stage was tilted until the imaged beam (on the CCD camera) does not change its central position when the x and y stages are moved.

Figure 4.1: The optical beam delivery layout a) immediately following the laser head and b) on a vertical slab for top-down laser processing. Stage motion is described by the x , y and z coordinate system.

For the experiments in Chapter 6 where an incident angle was required, a custom assembled mount was used (Figure 4.2). A Thorlabs AMA009 corner joint provided a level surface for sample attachment, and was bolted into a 360° rotational mount, attached to a plate base. Initially the mount is aligned at normal incidence and adjusted such that the back-reflection matches an incoming beam at Aperture A3. Tilt corrections

were performed by tightening the screws fixing the mount to the translational stage, and arranging spacers underneath mount edges until correction is achieved.

Figure 4.2: A custom angle mount to varying incidence angle for the s-polarization (left) and p-polarization states (right).

The sample mount in Figure 6.2 is limited in that it could not be perfectly oriented around the mount's rotational axis. Because no back reflection can be captured for a tilted sample with this arrangement, aligning laser beam waist precisely to the target surface was ambiguous, and required a different procedure of best focus determination. Error in the required focal adjustment for incidence angles up to $\theta_1 = 65^\circ$ meant empirical ablation studies would need to be performed for every sample to find the best focus. This would be inefficient and time consuming, and would impose potential for further error in positioning when the sample is removed and remounted. However, at low pulse energy (19% moderator efficiency), ablation plumes could be observed through protective eye-wear allowing the focus position in the thin-film to be found empirically to within $100\ \mu\text{m}$. As a fast, reliable method that did not require the removal of the sample from the mount for inspection, $100\ \mu\text{m}$ was a tolerable error compared with the large range in focal displacements used for feature fabrication. For the scope of this thesis precision in feature positioning is not required, though in industrial applications high-end angled optical delivery methods and precision angle mounts would allow sub-micron placement precision.

4.3 Sample Preparation - 1 μm SiO_x on a silicon Substrate

Thin-films of SiO_x grown to 1 μm thickness over substrates of polished phosphorus-doped (001) crystalline silicon wafers of 400 μm thickness by plasma-enhanced chemical vapour deposition were available for use. Wafers were diced by hand with a diamond scribe into 1 cm^2 samples and cleaned with lens tissue soaked in a dilute ethanol solution, dragged in one direction using a different section of lens tissue for each stroke. Sample surfaces were inspected with an optical microscope to confirm a good surface finish, and absence of dirt, dust or debris. Adhering samples with sellotape to microscope slides permitted flexible mounting for laser processing and diagnostic tools (optical and scanning electron microscopy). These microscope slides could then be fixed to the processing mounts by either magnets (Newport TTN80) or tape (Angle mount).

4.4 Characterisation of Laser Ablation site Morphology

4.4.1 Exposure Patterns

To facilitate comparison of varying exposure conditions, ablation sites were arranged in a rectangular grid. For both normal and angled fabrication, site-to-site spacing was controlled by constant value x and y movements of the translational stage. Focal displacement was altered through z displacement changes whilst shifting in the x direction across the grid and pulse energy was varied in the y direction, producing a range of fluence and spot size exposures on the sample films. 30 μm spacings between neighbouring features were sufficient to avoid any processing overlap, and 60 μm spacings between lines of constant pulse energy prevented ejection debris obstructing laser writing.

The sample was tilted in the y-z plane, and for angled exposures lines of constant pulse energy were separated by a projected $60/\cos\theta_1$. A vertical displacement (focal offset) of $z = 128\ \mu\text{m}$ was required in order to maintain constant focal displacement when moving down the slope of a sample to the next line of constant pulse energy.

4.4.2 Optical Microscopy

Given the time consumption and financial expenditure associated with SEM and FIB use, ablation sites were initially assessed by white-light optical microscopy (Olympus BX51) with $10\times$, $20\times$, $40\times$ and $50\times$ dry objective lenses. Exposure sites were selected for further analysis by observing colour and morphology changes in the optical images, which offer an initial indication of quantised ejection or interface damage. Detailed optical microscopy was performed when a sample was selected for SEM analysis. Common to all incidence angles, a transition from dark green to lime-yellow gave indication of delamination at SiO_x -Si interface, while formation of dark-brown bordered zones represented ejection of film segments, and white regions point towards the possible formation of intra-film cavities. Full film ejection was indicated by a light central region rounded by a thick dark-brown border, with no internal structure.

Features of ablation sites could sometimes be difficult to identify in an SEM, with exact position within the exposure site grid hard to determine at high magnification. Images were collected across the full processed area of the sample at both $10\times$ and $50\times$ magnification. These are then stitched together to form a complete optical microscopy map of the surface, with an initial collation at $10\times$ used to guide the higher magnification. Whilst lines of equal spot size are easy to track in an SEM for normal incidence samples, tilt-error induced shift in exposure patterns at high incidence angles make tracking difficult (as reported further in Chapter 6). Ablation sites could be matched with the high magnification optical microscopy composite during SEM, allowing careful recording of exposure conditions.

4.4.3 Scanning Electron Microscopy

Two scanning electron microscopes were used to analyse sample topography: a low resolution, variable pressure Hitachi SU3500 and a higher resolution Hitachi SU8230. The SU8230 was primary used owing to its greater resolution and low magnification mode which aided exposure site location. The detail and resolution in SEM images are not determined by the size of an electron beam but are heavily controlled by the size of an electron interaction volume within the material - which is dependant on electron accelerating voltage, and the atomic number of the sample material.

Since we concern ourselves with topographical images, secondary electron imaging is preferable. Secondary electrons are ejected from sample atoms following an inelastic collision with a primary incident electron. This emission is low energy, offers high resolution and has a surface signal that is heavily dependant on curvature, making secondary electron imaging ideal for topographic studies. Typically a depth resolution between 10–100 μm can be achieved, from a region the diameter of the material interaction volume. Two secondary electron detectors were available: an upper detector, located inside the microscopes lens column, and a lower detector, positioned at an angle to the sample. Better topographical contrast is offered by the lower detector.

An electron accelerating voltage of 0.5 kV was found to offer an optimisation between resolution and sample charging, with a normal probe current and the SU8230 condenser lens 10.

4.4.4 Focused Ion Beam (FIB) Machining

Whilst scanning electron microscopy is a useful tool for studying surface morphology, it provides little insight to internal structuring. A focused beam of ions, commonly from liquid metal ion sources (LMIS), can be used to both image and machine a surface on the nano-scale, enabling a cross-sectional view. Care was required as the FIB process is by design destructive, and ion implantation can alter surface quality. Typically FIB and

SEM systems are used in conjunction to machine and image a sample respectively. This project makes use of a combined Hitachi FIB-SEM NB5000 with a Gallium ion source. With angled SEM acquisition following FIB machining, cross-sections at a 58° incline were taken. SEM images were produced using a 2 kV accelerating voltage, and loosely match the sample charging performance of the Hitachi SU8230, though at a slightly reduced resolution.

The morphology of intent represents both quantized ejected structures, that form terraced trenches in the SiO_x and surface blisters the require precision cutting. These present challenges that must be considering in the FIB milling approached. For typical exposure sites, a trench is first cut in front of the site, into which debris from closer cuts can fall. This first cut was done with a selected 40-1-550 beam, where the first number refers to the beam energy, the second refers to the operational mode (0 is used to denote imaging, 1 for cutting) and the third refers to severity of the cut. An intermediate cut, with a 40-1-150 beam is used to approach the feature midsection, before a final 40-1-80 beam was used to fine tune the surface. Progressively softer machining was required to avoid melting sensitive and thin cross-sectional features - though the precise weighting of each stage is dependent on material properties and sample morphologies. For more delicate structures, a gentler cut was required with 40-1-30 and 40-1-15 beams used in 3 minute processing windows until the desired internal structure is revealed.

Chapter 5

Normal Incidence

In this chapter, the results of normal incidence laser exposure (θ_1) on 1 μm thick SiO_x thin-films with silicon substrates are presented. Here a range of pulse energies and spot size exposures are produced through laser irradiation, and assessed with optical microscopy, SEM and FIB cross-sectional imaging. Interference-driven quantized structuring is shown to produce multi-layered film blistering and a range of stacked intra-film micro- and nano-cavities. The novel surface topographies and internal structure discussed in this Chapter represent clear advancements in thin-film laser processing. The discussion provided therein forms a submitted journal paper, authored by the following: **David M. Roper**, Stephen Ho, Moez Haque, and Peter R. Herman.

5.1 Results of Normal Incidence Exposure

For the tight focus condition, $w_0 = 2.3 \mu\text{m}$, laser ablation sites were initially assessed by optical microscopy and morphology was inferred from thin-film interference color changes. Each exposure was trial three times, demonstrating process repeatability (for the beam and materials parameters outlined in this thesis) in order to rule out the influence of thin-film or interfacial defects. Figure 5.1a presents a composite optical micrograph of the laser exposure pattern formed, at a $10\times$ magnification. Here, pulse energy was fixed

for each row, varying from $1.03 \mu\text{J}$ (top) to $0.11 \mu\text{J}$ (bottom). Focal displacement was adjusted in steps of $5 \mu\text{m}$ across each row (site to site) to increase spot size and decrease fluence with respect to the central tight focus condition, marked by the dashed vertical line. This arrangement presents systematic trend lines to investigate the influence of both area and pulse energy on the quantized intra-film ejection process in a relevant exposure range from 6.19 J/cm^2 (top row) to 0.07 J/cm^2 (bottom row) of average fluence for the tight focus case in Figure 5.1a.

Figure 5.1: a) An optical micrograph ($10\times$ magnification) of $1 \mu\text{m}$ thick SiO_x film exposed with normally incident single laser pulses, on a $30 \mu\text{m}$ by $60 \mu\text{m}$ spaced grid, separated in zones of quantized film ejection (1), full film ejection (2) and interface-only modification (3). Pulse energy is fixed along each row (as shown) and focal displacement to increase spot size (bottom) is varied at $5 \mu\text{m}$ increments horizontally from the best focus ($w_0 = 2.3 \mu\text{m}$ on vertical dashed line) and highest fluence exposure. b) SEM image of select region of high pulse energy exposures and c) a magnified SEM image of a representative full film ejection site.

Following prior studies, similar energy-displacement exposure patterns have been beneficial to identify processing windows with distinct morphology that separate into zones

approximately along uniform fluence lines, leading to triangular shapes of different modification [17, 19, 42]. For the presented $1\text{ }\mu\text{m}$ SiO_x film, three distinct modification zones are shown in Figure 5.1a, separated by the overlaid red lines and labelled 1 to 3. The low-fluence exposure region below the blue lines in the bottom left and right corners in Figure 5.1a show the natural dark-green color produced by thin-film effects, where laser exposures were below the threshold for any material [17]. A color transition of dark green to lime-yellow was identified at a threshold fluence of $0.060 \pm 0.006\text{ J/cm}^2$, marked by the blue line positions, where exposure sites were found with a delaminated SiO_x interface. Here, no evidence of segment ejection is found and this zone is labelled 3 in Figure 5.1a. On increasing fluence, color shifted to a lighter hue on larger separation of the thin-film interface.

For a moderate pulse energy range ($0.04\text{ }\mu\text{J}$ to $0.24\text{ }\mu\text{J}$), a lower red V-line marks the transition from interface-only modification (zone 3) to quantized intra-film ejection (zone 1). Above this V-line, ablation sites showed dark-brown borders that indicated quantized ejection of film segments (verified by SEM later) to a pulse energy of $0.24\text{ }\mu\text{J}$. Full film ejection was driven with a higher pulse energy, defining a distinct zone 2, but presented a fluence threshold that varied with the beam spot size. For larger beam radii exceeding $3.7\text{ }\mu\text{m}$, only an abrupt transition from interface-only modification to full film ejection was identified without evidence of an intermediate zone of quantized ejection. However, the three morphology zones meet at the triple point seen at $0.24\text{ }\mu\text{J}$ pulse energy and beam waist radius of $3.7\text{ }\mu\text{m}$. This $3.7\text{ }\mu\text{m}$ radius represents the largest spot size for generating large-area quantized ejection in the present $1\text{ }\mu\text{m}$ thick SiO_x film. Above this energy ($0.24\text{ }\mu\text{J}$), the maximum radius for quantized ejection narrows, following the inverted red V-lines in Figure 5.1a, above which only full film ejection was observed. The full film ejection sites are identified by a light colored central region surrounded by a dark boundary of interface-only modification, marked with a lower pulse energy boundary having the W-shaped boundary (red lines) in Figure 5.1a. Interface-only (zone

3) and full-film ejection (zone 2) therefore narrowly limit the laser processing window for quantized intra-film ejection to the diamond-shaped zone 1, with pulse energy restricted from 0.04 to 0.76 μJ at tight focusing ($w_0 = 2.3 \mu\text{m}$ on vertical dashed line), and otherwise confined to a maximum radius of 3.7 μm at 0.24 μJ pulse energy.

Figure 5.1b shows a low magnification SEM image, selected from Figure 5.1a (black dashed square) to capture the inverted V-line boundary separating strong quantized film ejection in zone 1 (lower) from full-film ejection of zone 2 (higher). In zone 1, evidence of blisters, perforated blisters, and quantized ejection is seen in optical microscopy, although these features are better studied definitively at high resolution. Only bright images are identified in zone 2, representing fully ejected films, owing to the increased conductivity of silicon. A represented example is depicted in Figure 5.1c, which shows a magnified SEM image, at a fluence of $4.57 \pm 0.14 \text{ J/cm}^2$, at tight focus $w_0 = 2.3 \mu\text{m}$, of a full film ejection with remnants of SiO_x film segment surviving in centre beam zone. The fluence and pulse energy required to achieve full ejection at threshold line decreases with an increasing spot size, following the inverted V-line threshold, terminating at the triple point (0.24 μJ) as shown in Figure 5.1a. This presents a counterintuitive observation, that the transition from quantized ejection to full film ejection can be triggered by an increasing spot size. With the intra-film morphology presented in Figure 5.1a and 5.1b unclear, the remaining focus of this chapter lays in the assessment of zone 1 intra-film ejections (diamond shaped region) by high resolution SEM and FIB profiling.

Figure 2 presents a range of selected exposures, 0.50 J/cm^2 to 3.78 J/cm^2 , from modification zone 1 in Figure 5.1a at the tight focus condition, $w_0 = 2.3 \mu\text{m}$, which illustrate the sequence of intra-film blister formation, perforated blister, and ejected segments with increasing fluence. These sites were assessed by SEM and FIB cross-sectional imaging. Here selected exposures shown in Figure 5.2 present a detailed progression of sequential ejections from greater depths within the thin SiO_x film with increasing fluence. The 1st full segment ejection was observed at a threshold of $0.28 \pm 0.02 \text{ J/cm}^2$ (not depicted in

Figure 5.2), and here evidence of blister formation was not observed. The transition from single segment ejection to a blister forming from a second full segment, is seen between Figures 5.2a and 5.2b, when fluence was increased to $0.89 \pm 0.03 \text{ J/cm}^2$. Previously, few intra-film layer interactions have been noted for low fluence and low segment order, but here, FIB cross-sectional imaging reveals a novel multi-layered internal structure for the 2nd segment blister formed in Figure 5.2c at $1.11 \pm 0.04 \text{ J/cm}^2$. The 1st segment was ejected to a measured depth of $197 \pm 10 \text{ nm}$, which represents a slight deviation from the combined 0th and 1st segment prediction of 225 nm and may represent film thickness variation or thinning of the ejection wall. The prominent 2nd segment blister was measured to rise $500 \pm 10 \text{ nm}$ above the SiO_x film surface, enclosing an internal semi-spherical cavity of radius $610 \pm 10 \text{ nm}$ and wall thickness of $180 \pm 10 \text{ nm}$, which corresponds to an expected segment thickness of $\lambda/2n_{\text{film}} \cos \theta_2 = 176 \text{ nm}$. The internal structure thus reveals a stack of open micro-cavities forming with a $470 \pm 10 \text{ nm}$ height between both the 2nd and 3rd and, 3rd and 4th segments. Additionally, a $100 \pm 10 \text{ nm}$ height cavity is seen to open between the 4th and 5th segments. At the interface, a ring like cavity of $180 \pm 10 \text{ nm}$ height and $710 \pm 10 \text{ nm}$ annular radius was formed by the action of the central high laser fluence fusing together the 5th and 6th and pinned this fused pair to the silicon.

Figure 5.2: Low (left) and high (right) magnification SEM images of $1\ \mu\text{m}$ SiO_x films on silicon substrates exposed to a single femtosecond laser pulse at a wavelength of $515\ \text{nm}$ for increasing fluence exposures from (a) $0.50\ \text{J}/\text{cm}^2$ to k) $3.78\ \text{J}/\text{cm}^2$, together with complimentary FIB cross-sectional profiles for images on the right column that reveal an intricate internal structure of stacked micro-cavities.

With increasing fluence, the intra-film structuring penetrates deeper into the film, locked to the anticipated laser-induced plasma planes at the interference maxima presented in Figures 3.3.3 and 3.8. The observed threshold for 2nd segment partial ejection

is presented in Figure 5.2d, with a prominent 3rd segment blister filling the perforated opening, as revealed at a fluence of $1.15 \pm 0.05 \text{ J/cm}^2$. Here, topographical evidence for film delamination around a $5 \text{ }\mu\text{m}$ radius from the exposure centre point is also observed. Figure 5.2e (left) shows a fully formed expansion of the 3rd segment to form large diameter blister at a slightly higher fluence of $1.74 \pm 0.07 \text{ J/cm}^2$ rising to $1.92 \pm 0.010 \text{ }\mu\text{m}$ above the thin-film surface. The FIB cross-section in Figure 5.2e (right) reveals the peeling of the 2nd segment, flipped over covering most of the annular crater of ejected segments 1 and 2. The 3rd segment blister in Figure 5.2e (right) (distorted and perforated by ion bombardment) shows a cavity having opened to of $930 \pm 10 \text{ nm}$ with intact walls, with an estimated wall thickness of $80 \pm 10 \text{ nm}$, thinned by $2\times$ from the original segment thickness of $\lambda/2n_{\text{film}} \cos \theta_2 = 176 \text{ nm}$. A large internal cavity between the 4th and 5th segments has further opened to $1.04 \pm 0.010 \text{ }\mu\text{m}$ height. These multi-layered intra-film blisters have been connected centrally with the silicon, via the fused 5th and 6th segments. A larger annular ring has formed at the interface with $1.01 \pm 0.010 \text{ }\mu\text{m}$ radius and $210 \pm 10 \text{ nm}$ height, compared with a similar structure observed in Figure 5.2c. An intra-film ring cavity has also formed unbroken at $1.110 \pm 0.010 \text{ }\mu\text{m}$ diameter, opening by $30 \pm 10 \text{ nm}$ vertically between the folded 3rd segment and the 4th segment blister.

The perforation of the 3rd segment blister in Figure 5.2f at $1.82 \pm 0.07 \text{ J/cm}^2$ evolves with the formation of a large internal blister from the 4th segment as shown in Figure 5.2g, at $2.11 \pm 0.08 \text{ J/cm}^2$. Segment 3 in Figure 5.2f is significant in forming a thin walled cylinder, stretched and thinned from the expected 176 nm segment thickness, and positioned orthogonal to the thin-film surface. In Figure 5.2g, this opened 3rd segment blister appears to form a thinned nano-film “skirt” around the emerging 4th segment blister. Such 3D surface morphologies have not been previously documented. At similar fluence exposure, the 3rd segment skirt rose to $880 \pm 10 \text{ nm}$ above the surface as seen in Figure 5.2h (left). The FIB cross-section shown in Figure 5.2h has distorted the nano-

wall structure, but confirms a gap having opened against the inner 4th segment blister. A large $1.02 \pm 0.01 \mu\text{m}$ height micro-cavity is revealed between this 4th segment and lower 5th segment, and presents formation of stacked inner and connected ring nano-cavities formed by the sequential peeling and folding of segments.

The progression of larger blisters and inner-cavity structures as fluence increases in Figure 5.2, follows together with an increasing zone of interface damage rising from $5 \mu\text{m}$ diameter in Figure 5.2d to $6 \mu\text{m}$ in Figure 5.2g. At a higher fluence of $2.73 \pm 0.10 \text{ J/cm}^2$, one sees evidence of full film delamination in Figure 5.2i that progresses to partial ejection, finely connected to the silicon substrate in Figure 5.2j at $3.28 \pm 0.13 \text{ J/cm}^2$. Centrally, the 4th segment blister has expanded to a $2 \mu\text{m}$ diameter in Figure 5.2i, and then perforated to form a large skirt at the higher fluence in Figure 5.2j. These novel intra-film structures have formed over larger diameter film area of $\approx 8 \mu\text{m}$ where significant interface damage and thin-film fracture are evident. Figure 5.2k provides definitive assessment of this high-fluence morphology, revealing near full film ejection at an increased fluence of $3.78 \pm 0.15 \text{ J/cm}^2$. In Figure 5.2k (right), a remarkable $5.46 \pm 0.01 \mu\text{m}$ high micro-chamber of dumbbell shape has opened between the 4th and 5th segments. For the first time, intra-film blister formation opening both above and the thin-film layer is shown, to form this large chamber. Perforated and ejected blister segments are noted above the large chamber, while an annular nano-cavity ring is noted to have open periodically inside the ejected full film, at a larger radius ($\approx 1.7 \mu\text{m}$) encircling the open chamber. The fused 5th and 6th segments, define the walls of the bottom chamber and have been connected in this novel morphology to the silicon substrate at a centre base, with a protruding whisker of SiO_x ($2.34 \pm 0.010 \mu\text{m}$ in length) penetrating vertically into the chamber. Evidence of silicon melt under the radial driven ablation forces from a confined cavity is apparent below the structure on the silicon substrate. Mechanical cleaving by the ablation forces originating at the interface, propagating through the SiO_x also appears to be guided by $\lambda/2n_{\text{film}} \cos \theta_2$ quantized modification steps.

5.2 Discussion of Normal Incidence Exposure

Thin-film coloring effects observed by optical microscopy (Figure 5.1a) revealed the formation of three modification zones, previously unobserved in exposure patterns. The appearance of interface delamination (zone 3) and quantized ejection (zone 1) is as previously demonstrated in similar studies [2, 17, 19] but here the appearance of a novel region of full film ejection (zone 2) presents evidence for a new control parameter for engineering surface topographies. This full film ejection is confirmed by SEM imagery in Figure 5.1b, where a clear transition from quantized to full film ejection with an increase in focal displacement is highlighted, with a magnification of a representative exposure site provided in Figure 5.1c. This is an intriguing and counterintuitive observation, where the transition is controlled by an increase in spot size at constant pulse energy (a reduction in fluence).

The observations outlined in the results indicate a complex interaction at the film interface that is not yet fully understood. It is suggested that intra-film plasma planes not only shield the laser energy from reaching the interface, but also induce downward forces to weaken the confined interface interaction. In this way, full-film ejection is inhibited for small diameter beams, in the central high fluence exposure of the Gaussian beam shape. These effects are noted be less effective for large-diameter beams (i.e. left and right of diamond-shaped zone 1), where the expanding, heated thin SiO_x layers can become unstable at larger sizes, giving prominence to full film ejection (transition between zone 1 and 2 in Figures 5.1a and 5.1b).

One notes the observation of a large radius of interface modification at low pulse energies that appears more susceptibility to full film ejection. Interface modification can lead to delamination, or a weakening and stressing of the interface, which facilitates the propagation of interfacial fracture. The intra-film plasma disk explosions can further drive downward shock fronts that re-seal the delaminated interface zone (interface in Figure 5.1c). This implies a complex film geometry of time-varying dynamics, wherein expansion

of an intra-film cavity, for example between the 4th and 5th drives a downward shock front against the silicon substrate that manifests in the fusing of the 5th and 6th segments, and their combined re-connection with the substrate in Figure 5.2k). The resulting bending moment of such laterally cleaved multi-layered structures may be responsible for driving farther reaching intra-film fractures that extend the edges of delamination. Such bending moment effects will intensify with increasing laser spot size, following the growing size of the interface weakening or delamination effect. Examining the border between the quantized ejection morphology (zone 1) and full film expulsion (zone 2) indicated by the red line in Figure 5.1a, we note a range over which this transition is possible. For each pulse energy between 0.24 μJ and 0.76 μJ , there exists at spot size radius between 2.3 μm and 3.7 μm (Focal displacement between 0 and 30 μm) at which full film ejection will occur. At higher pulse energies smaller spot sizes are required to achieve full film ejection, with the driving forces between the expanding intra-film plasma disk explosions growing faster and taking precedence over the interface explosion with increasing pulse energy.

The W-shaped transition zone (red line) in Figure 5.1 revealed a high sensitivity of the full film ejection threshold fluence to the laser spot size, permitting a new way to control whether quantized intra-film ejection and full film ejection will compete and dominate in determining the final film morphology, without the use of angled incidence and polarization states. In this way, the transition can be achieved without feature ellipticity or the additional complexity involved with aligning samples at high incidence angles. Hence, re-positioning of the laser focus is a simple means to vary area and rapidly switch morphology between different ejection regimes in multi-purpose single step laser fabrication applications. Further study may show that similar means of areal exposure plays a role in controlling the number of intra-film segment ejections, independent of the fluence or pulse energy variation presently evident in Figures 5.1 and 3.3.3.

Close examination of the intra-film quantize within the diamond shaped zone 1, Fig-

ure 5.2 presented a detailed examination of the morphology progression for quantized ejection in zone 1 at the tight focus condition $w_0 = 2.3 \mu\text{m}$. These results were significant in demonstrating the formation of layered intra-film blisters, with stacked micro- and nano- cavities within a thin, $1 \mu\text{m}$ SiO_x film. This internal structure can be clearly seen in the FIB cross-section shown Figure 5.1c. These observations point to the occurrence of near simultaneous and balanced nano- plasma disk explosions, with shock fronts propagating through the thin-film layer. Complex competing dynamics drive the expulsion of material, with solid flow and melt hydrodynamics leading to a range of novel features. The formation of large, spherical blisters with thicknesses stretched to less than the modelled 176 nm segment thickness was presented in Figure 5.2e and is indicative of the interplay between segment expulsion and melting. The bursting of these structures to form vertical walls (Figure 5.2f) and attached border “skirts” (Figure 5.2i) is evidence of the extreme conditions present shortly following laser irradiation, yet manifesting in delicate nano-glass cylindrical or spherical structures.

At higher fluence (3.78 J/cm^2) the aggressive explosion of stacked plasma disks was demonstrated in the formation of a novel chamber by bi-directional expansion of the cavity formed between the 4th and 5th segment (Figure 5.2K). Evidence of intra-film cleaving aligned with steps matching thin-film interference presents evidence for guided fracture through low intensity modification at the exposure site perimeter. The expansion of the intra-film chamber against the silicon substrate drove the propagation of fracture along the interface and through the film. The confined phase explosion opening this large chamber may dominate overall at this fluence exposure, overpowering the interface interaction as well as fusing of the 5th and 6th segments to each other to pin down the silica film in this novel small area zone. The complex hydrodynamics of opening silica layers in various degrees of non-equilibrium states, and liquid to solid states of extreme temperature gradients, and various viscosity are further evident in the flow of silica melt above the 5th segment, pushed centrally upward into the chamber, and solidifying on

cooling to form a whisker (< 300 nm diameter).

The novel 3D nano-structures presented in this thesis represent exiting advancements not previously demonstrated with laser surface structuring. In their fabrication, these features meet the expressed goal of this thesis, discussed in Chapter 1, to improve and expand existing controls on thin-film topographies and intra-film structuring. Manipulating surface topographies to form non-planar membranes, with unique 3D shape variations would be beneficial to a wide range of applications. Tuneable surface topographies find particular relevance in biological study with micro- and nano-topographies presenting controlled ways to interact with cellular environments, where the novel 3D features demonstrated in this thesis may be useful in stimulating stem cell differentiation [7]. The demonstrated stacked micro- and nano-cavities may find application in the production of optical nano- or micro-resonators [50] where the direct write process would allow rapid placement in a thin-film layer above a photonic chip. The thinned vertical wall formation shown may also allow the creation of MEMs sensing surfaces, with future development targeting cantilever vibration or output through blister deformation, in geometries not possible in conventional lithographic techniques. Additionally the process of forming ultra-thin spherical blisters of silica could be favourable to harness whispering gallery mode optics to develop sensing applications ranging from force and temperature, to gas and bio-sensing [51].

Chapter 6

Angled Incidence

In contrast to the results presented in Chapter 5 where exposure sites were irradiated at normal incidence, in this chapter, the results of angled laser exposure (θ_1) on 1 μm thick SiO_x thin-films with silicon substrates are presented. The express purpose of this discussion is to investigate the effects of angle and polarization control on thin-film fringe visibility and the resulting surface morphologies. Here the simulations of Chapter 3 and compared with results, following the method outlined in Chapter 4. The discussion provided therein forms a submitted journal paper, authored by the following: **David M Roper**, Stephen Ho, Moez Haque, Prasoon Jha and Peter R Herman.

6.1 Results of Angled Incidence Exposure

For the tight focus condition, $w_o = 2.3 \mu\text{m}$, laser ablation sites were first assessed by optical microscopy, where color changes were used to infer feature morphology according to thin-film interference effects [17]. Figure 6.1 displays optical micrographs of the exposure patterns formed for the s- and p-polarization states (Figures 6.1a and 6.1b, respectively) for incidence angle of $\theta_1 = 65^\circ$. Each row represents a fixed pulse energy, varying from 1.6 μJ (top) to 0.18 μJ (bottom). The average fluence exposure decreases from 4.13 J/cm^2 (top) to 0.48 J/cm^2 (bottom) along this line, and falls laterally on each

row before ending at a similar modification threshold. Focal displacement is shown to be varied across each row, leading to an increasing spot size and decreasing fluence exposure with deviation from the centre focus position.

This tight focussing ($w_o = 2.3 \mu\text{m}$) condition is marked by the dotted line shown for both polarization states, and is found to drift owing to sample tilt alignment error. Maximum incident angle was limited to a sample tilt of 65° with the use of a low NA lens due to geometric restrictions. The measurement of spot-to-spot separation indicated a corrected sample tilt angle of $63 \pm 1^\circ$ for p- polarisation and $64 \pm 1^\circ$ for s- polarisation. The remaining alignment error arose principally from the target azimuthal uncertainty with respect to the axis of the horizontal motion stage used to shift the sample along each column in the figure. A site-to-site (A to B) vertical displacement (focal offset) of $z = 128 \mu\text{m}$ (Figure 6.2) was required to maintain constant focal displacement and a deviation of $\approx 5 \mu\text{m}$ in the intended axial focus shift was observed - labelled as Δz in Figure 6.2. Since focal displacement is varied by $5 \mu\text{m}$ between features, which are spaced by $30 \mu\text{m}$, we see a physical shift of $30 \mu\text{m}$ when comparing the best focus of feature rows down the sample slope. The angular tilt of the best focus line in Figure 6.2b displays this combed error.

To better assess the morphology with the colour changes in Figures 6.1a and 6.1b, SEM and ion milling were matched with the following observational trends. A transition from dark green to lime-yellow gave indication of delamination at the SiO_x -Si interface (Figures 6.1e and 6.1f), while formation of dark-brown bordered zones represented ejection of film segments (Figure 6.1c), and white regions pointed towards the possible formation of intra-film cavities. Full-film ejection was indicated by a light central region rounded by a thick dark-brown border (Figure 6.1d), without showing additional structure in the spot centre.

In prior study, 515 nm laser exposure of SiO_x thin-films has been initially presented for normal incident angle [2], with quantized intra-film ejection verified for $3.5 \mu\text{m}$ thick

Figure 6.1: Optical micrographs ($10\times$ magnification) of SiO_x film, exposed at $\theta_1 = 65^\circ$ with a) s-polarized and b) p-polarized single laser pulses on a $30\ \mu\text{m}$ by $60/\cos(\theta_1) = 140\ \mu\text{m}$ spaced grid, with pulse energy fixed along each row (as shown), and a $5\ \mu\text{m}$ focus displacement shown horizontally. The dashed line indicates the best focus position (i.e. highest fluence exposure) for each row. At $50\times$ magnification, expanded views of c) quantized ejection at the s-polarization state and d) full film ejection for the p-polarization state, each at incidence fluence of $3.27 \pm 0.29\ \text{J}/\text{cm}^2$, in contrast with interface delamination (lime-yellow coloration) recorded at e) $0.099 \pm 0.011\ \text{J}/\text{cm}^2$ fluence for the s-polarization state and f) $0.11 \pm 0.012\ \text{J}/\text{cm}^2$ for the p-polarization state.

films through SEM and ion milling. Because film thickness strongly affects the intensity patterns and laser interaction, the fluence thresholds for generating intra-film ejections (i.e. 1st, 2nd, 3rd segments), and interface modification were assessed in chapter 5 for the case of normal incident irradiation of $1\ \mu\text{m}$ thick SiO_x film. Table 6.1 presents the fluence thresholds, for comparison, observed to mark the onset of SiO_x -Si delamination, and 1st segment, 2nd segment, and full film ejection, with values of $0.063 \pm 0.007\ \text{J}/\text{cm}^2$, $0.28 \pm 0.02\ \text{J}/\text{cm}^2$, $1.14 \pm 0.08\ \text{J}/\text{cm}^2$ and $3.92 \pm 0.27\ \text{J}/\text{cm}^2$, respectively. These thresholds for normal incidence ($\theta_1 = 0^\circ$) are further evaluated for the case of s- and p-polarized light incident at $\theta_1 = 65^\circ$, following similar optical microscopy (Figure 6.1), SEM (Figure 6.3), and ion-milling analyses (Figure 6.4).

Figure 6.2: a) Schematic side view of a sample surface tilted at incident angle of θ_1 , with focal offset scaling as $z = y \tan(\theta_1)$ (point B) and focal offset error given by $\Delta z = y(\tan(\theta_1 + \Delta\theta_1) - \tan(\theta_1))$, owing to angular tilt error $\Delta\theta$.

The onset of any observable morphology at lowest fluence is marked by the outer perimeter of the exposure grids shown in Figure 6.1. This perimeter established the threshold fluence of $0.11 \pm 0.012 \text{ J/cm}^2$ (Table 6.1) defining the onset of interface delamination for p-polarized exposure, as shown at $50\times$ magnification in Figure 6.1f. By tracking the dashed line of tightest focus in Figure 6.1, full film ejection (representative example given in Figure 6.1d) is noted at all sites from the top to the bottom row, with the bottom row marking a threshold for full film ejection of $0.48 \pm 0.05 \text{ J/cm}^2$ (Table 6.1). Interface damage (i.e. Figure 6.1f) was identified below this fluence exposure (i.e. 0.11 to 0.48 J/cm^2 range), while full-film ejection was only observed without indication of quantized intra-film ejection in optical microscopy above this fluence (i.e. 0.48 to 4.11 J/cm^2 range). This full film ejection threshold (0.48 J/cm^2) contrasts with the significantly higher value of $3.92 \pm 0.27 \text{ J/cm}^2$ observed at normal incidence.

Figure 6.3 introduces the SEM images recorded at SiO_x ablation sites for s- and p-polarization. For the p-polarization state (Figure 6.3a left), the interface modification presented by optical microscopy (i.e. indicated by lime-yellow color change in Figure 6.1) in the exposure range of 0.11 ± 0.012 to $0.48 \pm 0.05 \text{ J/cm}^2$ was difficult to observe by SEM and is not reported. The SEM imaging shows full ejection of the SiO_x film for

Table 6.1: Fluence threshold values for the onset of interface delamination, 1st segment, 2nd segment and full film ejection, and relative intensities at associated fringe maxima and interface positions.

	$\theta_1 = 0^\circ$	$\theta_1 = 65^\circ$	
Fluence Threshold (J/cm ²)			
Polarization	<i>linear</i>	<i>s</i>	<i>p</i>
Interface Delamination	0.063 ± 0.007	0.099 ± 0.011	0.11 ± 0.012
1 st Segment	0.28 ± 0.02	0.63 ± 0.05	x
2 nd Segment	1.14 ± 0.08	1.08 ± 0.08	x
Full film Ejection	3.92 ± 0.27	$> 4.11 \pm 0.29$	0.48 ± 0.05
Relative Intensities			
Fringe Maxima	2.30	1.45	0.65
Interface	0.275	0.14	0.48

fluence increasing from 0.75 J/cm² (Figure 6.3a) to 2.17 J/cm² (Figure 6.3e) exposure, corresponding to the optical micrographs in Figure 6.1b enclosed in red circles on the tight focus line. The 1 μ m deep wells were opened against a silicon base, as verified by EDS. silicon surface melting effects are noted to have been driven from a strongly confined SiO_x-Si interface interaction. Similar full film ejection was confirmed over a wider fluence exposure, beginning with the full film ejection threshold of 0.48 J/cm² (Table 6.1) to the maximum value tested at 4.11 J/cm², and encompassing the wide range of tight focusing to large-area sites shown in Figure 6.1b. The ejection sites were relatively large (i.e. 7 $\times$ 15 μ m in Figure 6.3a left) in contrast with the laser spot size ($w_o = 2.3 \mu$ m), attesting to a high threshold for interface ejection of the whole film thickness that includes mechanical cleaving forces as noted by the sidewall morphology in the SEM images.

With the absence of intra-film modification for the presently examined p-polarized data, the 1st and 2nd intra-film ejection thresholds were marked “x” in Table 6.1 between the fluence thresholds for interface damage and full-film ejection. The SiO_x-Si interface interaction for this high incident angle ($\theta_1 = 65^\circ$) is therefore observed to be fully dominant over the intra-film plasma disk formation physics.

Figure 6.3: a) SEM images (at the same magnification) of $1\ \mu\text{m}$ SiO_x films on silicon substrates exposed to a single femtosecond laser pulse at a wavelength of 515 nm and $\theta_1 \approx 65^\circ$ tilt angle for increasing fluence exposures of a) $0.75\ \text{J}/\text{cm}^2$, b) $0.92\ \text{J}/\text{cm}^2$, c) $1.12\ \text{J}/\text{cm}^2$, d) $1.59\ \text{J}/\text{cm}^2$, and e) $2.17\ \text{J}/\text{cm}^2$ for p- (left) and s- (right) polarizations. For a spot size of $4.6\ \mu\text{m}$ the 1st, 2nd, and 3rd intra-film segment ejections are shown to be ejected with increasing fluence exposure for s-polarized light, whereas complete film ejection is shown for p-polarized light, with no evidence of quantized ejection.

Returning to the optical microscopy introduced in Figure 6.1, the onset of $\text{SiO}_x\text{-Si}$ delamination was identified at a threshold fluence of $0.099 \pm 0.011 \text{ J/cm}^2$ (Table 6.1) on the outer perimeter of ablation sights for the s-polarisation state (Figure 6.1a). An interference-based color change to lime-yellow indicates separation at the thin-film interface as presented in Figure 6.1e with $50 \times$ magnification. Unlike the p-polarization state, full film ejection was not observed along the line of tightest focus in Figure 6.1a (dashed line). However, the dark-brown bordered zone was indicative of quantized ejection, with Figure 6.1c being a representative example of multi-segment ejection recorded with $50 \times$ magnification for a 3.27 J/cm^2 exposure. Such quantized intra-film effects are strongly evident while apparent tracking along the line of tight focus to a low fluence of 0.75 J/cm^2 . At the highest exposure fluence (top line) of $4.11 \pm 0.29 \text{ J/cm}^2$, full film ejection was not apparent in optical microscopy. In order to more precisely identify the 1st segment ejection threshold and follow the number of ejection layers with increasing fluence, SEM analysis is necessary.

In SEM analysis of key ablation sites in Figure 6.1a, a 1st segment ejection threshold of $0.63 \pm 0.05 \text{ J/cm}^2$ was established for the s-polarization state. Figure 6.3 (right) highlights representative SEM images for a selected range of exposures that are highlighted in Figure 6.1a (circled in red) and presented for comparison with ablation sites exposed in the p-polarisation state at the same fluence exposures (Figure 6.3 left). The progression for the s-polarization state (Figure 6.3 right) is comparable to that seen previously for normal incidence [2], but is deeply contrasting with the images shown for the p-polarization state (left) in both size and morphology. Whilst full-film ejections were driven over large areas of $\approx 15 \text{ }\mu\text{m}$ diameter for the p-polarization state, the intra-film ejections for s-polarization were significantly smaller, ranging from $5 \text{ }\mu\text{m}$ to $10 \text{ }\mu\text{m}$ for the same fluence exposure range.

Close examination of the SEM images for s-polarization definitively reveals the first segment ejection (Figure 6.3a right) for the $0.75 \pm 0.05 \text{ J/cm}^2$ fluence example, with in-

creasing fluence exposure generating a 2nd segment ejection at $1.1 \pm 0.08 \text{ J/cm}^2$ (Figure 6.3c right) and a 3rd segment ejection at $1.59 \pm 0.11 \text{ J/cm}^2$ (Figure 6.3d). The 1st and 2nd segment fluence values are included in Table 6.1. The sequence of peeling deeper segments spaced by $\lambda/2n_{\text{film}}\cos\theta_2$, with increasing fluence, was apparent when observing the remaining evidence of segment steps at the edges of ejection sites and demonstrates reproducible control over the segment ejection number as previously reported for Si_3N_4 thin films [17]. The effect of sample tilt angle is further evidenced in the SEM images (Figure 6.3) by intra-film ejection zones that were elongated to 1:2.4 ellipticity [18] according to the 1: $1/\cos(65^\circ)$ ratio expected for the projected beam. This elongation was further modified in the case of s-polarization with a lateral asymmetry along the tilt axis (left-to-right) in Figure 6.3 (right). The morphology of the intra-film ejections are more distinctly driven from the right side, corresponding to the laser beam exit direction, where intra-film segments are peeling from right to left in the images (i.e. Figure 6.3e). The number of ejected segments also varies asymmetrically across the exposure spot. This effect is less apparent for p-polarized exposures (Figure 6.3 left).

To study these asymmetric effects further, focussed ion beam milling and SEM cross-sectional imaging of select samples were carried out, yielding a representative image for s-polarized intra-film ejection in Figure 6.4a. This sample from Figure 6.3c displays a full 1st segment ejection with thickness of $190 \pm 10 \text{ nm}$, a nearly full ejection of the second segment with $220 \pm 10 \text{ nm}$ thickness, a fused 3rd and 4th segment of a combined $450 \pm 10 \text{ nm}$ thickness, and a remaining thinner bottom segment of $130 \pm 10 \text{ nm}$ thickness above the interface. This spacing closely resembles the fringe spacing shown in Figure 3.7, with high intensity laser disks clearly delimiting the segment layers as seen in Figure 6.4a. Shock front competition amongst several stacked micro-plasma disk explosions is anticipated to have fused the 3rd and 4th segments that initially would have cleaved open by the laser plasma formation. The opening of a $400 \pm 20 \text{ nm}$ high intra-film cavity is observed between the fused 3rd/4th segment and the bottom remaining section of the

film. The 2nd ejected segment thickness (220 ± 10 nm) matches the $\lambda/2n_{\text{film}}\cos\theta_2 = 225$ nm fringe spacing within the measurement error of ion-milled SEM imaging. This spacing represents a 20% thickness increase compared with samples irradiated at normal incidence. The cross sectional imaging therefore verifies the inter-film laser cleaving at interference maxima.

Figure 6.4: A comparison of a) SEM and FIB cross-sectional imagery with b) lateral fringe visibility variation in a 1 μm SiOx thin film on a Si substrate for a 515 nm wavelength s-polarized Gaussian pulse, with a beam waist radius of 2.3 μm , fluence of 1.12 J/cm², incident at a 65° angle, from left to right. $1/e^2$ intensity positions are indicated by the red dotted lines.

The lateral asymmetry in intra-film ejection in Figure 6.4a is assessed against the asymmetric visibility profile previously presented for s-polarization in Figure 3.7c. The lateral visibility variation (Figure 6.4b) is scaled in size and aligned with the SEM and cross-sectional FIB images (Figure 6.4a). Only one segment is shown to be completely ejected at position A, aligning with the lower fringe visibility expected on the left. In contrast, a sharp removal of both the 1st and 2nd segments is noted in the centre and right

side (position B), corresponding with the higher fringe visibility in this beam exposure area. For size scaling, the vertical red dashed line marks the beam radius at $1/e^2$ intensity ($w_o/\cos \theta_1$).

6.2 Discussion of Angled Incidence Exposure

The presented results in this chapter are significant in demonstrating angle and polarization control of nonlinear optical interference for femtosecond laser nanostructuring of thin dielectric films, meeting the aims and goals of this thesis outlined in Chapter 1. In Figure 3.3.2, a visibility control of intra-film interference contrast was proposed by tuning the incidence angle and polarization state. A large incident angle of 65° was targeted to enhance visibility from 0.79 at normal incidence to 0.86 for the s-polarization state, or to dramatically diminish visibility to 0.16 for p-polarized light.

The effect of Gaussian beam walk-off on fringe visibility was further evaluated in the presented case of tight focusing ($w_o = 2.3 \mu\text{m}$) in thin film, suggesting a maximum film thickness condition (Equation 3.2) of $1.7 \mu\text{m}$ for degraded fringe visibility. The spatial variation of the Gaussian beam interference was evaluated by an FDTD model (Figure 3.7) for a lower $1 \mu\text{m}$ film thickness, yielding a sufficiently strong but laterally varying fringe visibility (Figure 3.7c) that was promising to test experimentally for quantized intra-film ejection. However, following the fringe maxima located closest to the silicon substrate, the visibility varied between 0.6 and 0.97 at the $1/e^2$ intensity (Figure 3.7) for this tight focusing case, that predicted the lateral asymmetry in quantized film ejections shown in Figure 6.4. The FDTD modelling also produced highly contrasting values of 1.45 and 0.16 for the relative fringe intensity maxima and 0.14 and 0.48 for the relative interface intensity for the s- and p-polarization states, respectively, which are summarized in Table 6.1 to compare with the highly contrasting surface morphology found experimentally for the s- and p-polarization states in Figures 6.1 and 6.4.

Thin-film coloring effects by optical morphology (Figure 6.1) indicated quantized intra-film ejected structures for s-polarized light, while otherwise demonstrating an abrupt transition from interface damage to full film ejection for the p-polarization state. Together with SEM imaging and ion-beam milling, fluence exposure windows were established for the onset of interface damage or delamination, and followed to higher fluences to distinguish the onset of quantized intra-film ejection from full-film ejection as summarized in Table 6.1 for the three cases: normal incidence linear polarization, angled incidence s-polarization, and angled incidence p-polarization. These onset fluence exposures for interface delamination, and 1st segment, 2nd segment, and full film ejection, are assessed against the relative intra-film intensities calculated for fringe maxima and interface positions.

The threshold for interface delamination (Table 6.1) increased by ≈ 1.5 times with angle to 0.099 ± 0.011 J/cm² and 0.11 ± 0.012 J/cm² for s- and p-polarization, respectively, relative to the normal incidence value of 0.063 ± 0.007 J/cm². These trends do not follow those predicted by relative intensity (2.3, 1.45, and 0.65 for normal, s-, and p-polarization, respectively), possibly owing to a strong polarization effect in the non-linear regime of high intensity laser light with the generated plasma disk [52]. For full film ejection, a much higher threshold fluence (≈ 8) was observed at normal incidence compared with the 0.48 J/cm² threshold seen for p-polarized light at an incidence angle of $\theta_1 = 65^\circ$. This contrast may be underpinned by the respective 2-fold decrease in relative intensities predicted at the interface (Table 6.1). However, empirically, the 8-fold decrease in threshold fluence suggests a more complex role of competing intra-film and interface ablation dynamics for s-polarization while intra-film dynamics were predicted to be much weaker, both in intensity peak and fringe visibility for p-polarization. Full film ejection was not observed for the s-polarization case to the upper exposure limit tested (4.11 J/cm²), which was otherwise sufficient (i.e. 3.92 J/cm²) for full film ejection in the normal angle case, possibly owing to the strong 2-fold decrease in the relative intensi-

ties predicted at the interface (0.14 versus 0.275) for the respective s-polarization state compared with normal incidence. These observations fulfil the experimental prediction outlined in Chapter 3 (section 3.5).

The SEM images in Figure 6.3 for high angle exposure (65°) presented definitive evidence of quantized intra-film ejection only for the s-polarized state, with morphology revealing 1st, 2nd, and 3rd segment ejection, and deeper intra-film cleaving effects (Figure 6.4a). In contrast, intra-film cleaving effects were fully inhibited with this high angle for p-polarized light. This result demonstrates a clear command and categorically shows the key role of angle and polarization for fringe visibility control in the processing of quantized ejections within thin-films. Further, their effect in enhancing or inhibiting the otherwise weakly interacting SiO_x film against the strong substrate (silicon) absorption at interface has been shown. The lack of observed quantized intra-film ejection at any fluence or spot size exposure for the p-polarization state leads to the conclusion that a fringe visibility of 0.16 (Figure 3.7) is below a critical threshold such that interface threshold will always been reached before intra-film ejection at fringe maxima can occur, as predicted in Chapter 3 (section 3.5). In this way, a visibility of 0.16 represents a lower bound for this critical visibility and experimentation at smaller incidence angles is required to better determine this transition condition.

Finally, the experiments demonstrated an expected increase in the intra-film segment thickness from 180 nm at normal incidence to 230 nm with angled s-polarized light, confirming facile sub-micron controls in the intra-film cleaving morphology and fulfilling the experimental prediction stated in Chapter 3 (section 3.5). The first physical evidence for a novel asymmetric cleaving morphology was also presented in Figure 6.4, inferred to arise from fringe visibility changes in the beam walk-off effect that must not exceed the condition presented in Eq. 3.2, and predicted by simulations discussed in Chapter 3. At the exposure site presented in Figure 6.4, high visibility is proposed to enhance intra-film ejection asymmetrically to the right side (position B) of the laser centre, while

lower visibility on the left (point A) inhibits formation of sharp plasma disks, reducing the number of ejection layers. This visibility contrast control represents an exciting new development that has potential to allow fine control over light confinement, influence ejection dynamics, or tailor melting. The intricate morphologies presented in Chapter 5 represent exciting surface features which may be harnessed for significant industrial application. In the demonstration of angle-control, the possibility to modify these structures is opened, to create, for example, aspherical blisters and elliptical wall cylinders in thin-dielectric materials.

With the underlying visibility control understood, the possibility of multi-purpose laser fabrication through complimentary intra-film and interface dominated processing provides the opportunity to tailor microtopographies to nanoscale precision with angle, polarization, film thickness, and beam size controls. The introduction of an angle driven lateral asymmetry in interference contrast may find relevance in the production of terrace microtopography when paired with angled segment thickness adjustment for supporting applications such as microbial interaction [53]. Through visibility enhancement with angle and a greater understanding of topographical control, the techniques discussed in this thesis pave a path towards tailoring quantized processing through demonstration of novel 3D surface topographies, and presents a promising extension of these phenomena into low index contrast film systems. In this way, the aims of this thesis outlined in Chapter 1 have been met.

Chapter 7

Conclusion

7.1 Summary

The control and demonstration of novel surface morphology and intra-film modification, outlined in this thesis, represents significant progression on the prior work existing in the area of thin-film processing. This thesis has demonstrated several advancements in the application and understanding of the nonlinear optical laser interactions that underpin the interferometric quantized ejection process inside transparent film. With exposure at normal incidence, novel 3D nano-structures have been fabricated in 1 μm SiO_x on silicon substrates. Quantized ejections to form blisters have been shown at increasing fluence, sequentially perforating to form thin orthogonal “skirt” and wall topographies that were not possible to fabricate by any previously known means. For the first time, an internal structure of stacked micro-cavities has been shown to form at quantized interference maxima. Additionally, laser spot size effects have been demonstrated, revealing a previously unobserved transition from quantized ejection to full film ejection on the increase of focal displacement. These 3D internal and topographical modifications represent exciting promise for a range of applications such as functional surface control, MEMs sensing surfaces and optical resonators. Additionally the formation of stack intra-film cavities

is promising in the creation of staged time-release drug membranes, but this application would required significant further development.

Polarization state and incidence angle were proposed as methods to manipulate Fresnel reflection coefficients and fringe visibility in a selected SiO_x on silicon system. In this thesis they have been shown to be powerful tools in tailoring the quantized ejection process through manipulation of intra-film relative intensities and fringe visibility. In order to study high angle effects and discuss extension of these methods to thicker films, a Gaussian beam walk-off effect was introduced as a limiting factor for thin-film interference with tightly focused laser beams.

A $1\ \mu\text{m}$ SiO_x film thickness was successfully used at a high incident angle of 65° to enable quantized intra-film ejection for s-polarized light with slightly enhanced visibility, or to otherwise inhibit intra-film cleaving effects for p-polarized light by highly diminished fringe visibility. The beam walk-off effect further manifested in a visibility variation across the small beam focus, introducing new asymmetry effects to control the intra-film cleaving morphology. Such angle tuning also presented the expected fine control of ejection layer thickness ($\lambda/2n_{\text{film}}\cos\theta_2$) for the first time. In this way, these observations validate the experimental predictions made in Chapter 3.

The analysis and concepts presented in this thesis advance new means for controlled precise ablation, melting and intra-film nano-structuring, together defining a highly facile and single-step process of ultrafast laser fabrication that can be scaled to large processing area and high speed due to the single pulse exposure. Moreover, the angle manipulation of the Fresnel reflection points to a valuable extension of this quantized intra-film phenomena to new material combinations with lower refractive index contrast that were previously unsuitable due to the interference limits of normal incident exposure.

7.2 Future Directions

It is suggested that modelling, experimental methods and observed results seen in Chapters 3, 4 and 6 be built on by seeking new thin-film systems to process with-in, with an emphasis on selecting materials with interesting application. The extension of quantized processing to low index contrast thin-film and substrate combinations would represent a significant milestone in the progression of the Interferometric Ejection technique to industrial relevance in, for example, the areas of medical, security and sensing. Furthermore, a study of finer fluence steps is required to better quantify segment ejection thresholds, with an additional project suggested to investigate the limits of film thickness on the angled modification shown in this thesis. The quantized blister structures introduced in Chapter 5 represent an interesting surface topography that would benefit from future study. Deformation modelling, analysis and experimentation is required to test the mechanical properties of these structures, and is crucial in assessing future applications of the features introduced. A study into the plasma physics and mechanical forces leading to spot size dependant full film ejection is also required to further understanding and control over these methods of intra-film modification, and develop techniques to reduce interface damage. Micro- and nano-structuring in the substrate may be employed in the future to manipulate the thermal constants at film-interfaces, and provide additional control through the optimization of thermal diffusion away from exposure sites. Repeating the findings outlined in this thesis in bioactive glasses would allow significant progression into the biomaterials field, in particular the structuring of drug-activated thin-films for temporal release time variation to surrounding tissue. In order to fully fulfil the potential for the fabrication techniques discussed in this thesis, a multi-disciplinary collaboration may be required.

Appendix A

Plane Wave Model

Included in this Appendix are the Matlab scripts contributed by Dr. Moez Haque to simulate thin-film interference, presented in Chapter 3.

A.1 Thin-film interference intensity

```
1 % Title: FPI_01_Basic_Plotter
2 % Author: Moez Haque
3 % Date Created: November 29, 2016
4 % Description: Outputs spatial intensity profile within a Fabry
   Perot for
5 %               TE and TM polarizations.
6
7 clear
8 clc
9
10 %% User Input
11 Theta_1_deg = 0; % Wave vector incident angle, degrees
12
```

```

13 Lx = 1;           % FPI wafer thickness , Microns
14 Ly = 1;           % Transverse length , Microns
15
16 lambda = 0.515;    % Free Space Wavelength , Microns
17 m_max = 10;        % Number of FPI pass orders to add
18
19 n1 = 1.0;           % Refractive Index , Medium 1
20 n2 = 1.46;          % Refractive Index , Medium 2 (complex
    allowed)
21 n3 = 4.22 + 0.038i; % Refractive Index , Medium 3
22
23 mu_r_1 = 1;         % Relative Permeability , Medium 1
24 mu_r_2 = 1;         % Relative Permeability , Medium 2
25 mu_r_3 = 1;         % Relative Permeability , Medium 3
26
27 dx = 0.00001;      % Discrete Space Step , Microns
28 dy = 1;             % Discrete Space Step , Microns
29
30 %% Pre-Calculations
31 epsilon_0 = 8.8541878176*10^(-12); % Permittivity of free space
32 mu_0 = 1.25663706 * 10^(-6);       % Permeability of free space
33
34 eta_n1 = sqrt( mu_r_1^2 * mu_0 / n1^2 / epsilon_0 ); %
    Impedence
35 eta_n2 = sqrt( mu_r_2^2 * mu_0 / n2^2 / epsilon_0 ); %
    Impedence

```

```

36 eta_n3 = sqrt( mu_r_3^2 * mu_0 / n3^2 / epsilon_0 ); %
    Impedence
37
38 Theta_1 = Theta_1_deg / 180 * pi;          % Propagation angle ,
    medium 1
39 Theta_2 = asin( n1*sin(Theta_1)/n2 );      % Propagation angle ,
    medium 2
40 Theta_2_deg = Theta_2 / pi * 180;          % Propagation angle ,
    medium 2
41 Theta_3 = asin( n2*sin(Theta_2)/n3 );      % Propagation angle ,
    medium 3
42 Theta_3_deg = Theta_3 / pi * 180;          % Propagation angle ,
    medium 3
43
44 Dy = Lx*tan(Theta_2);    % y-axis displacement from each pass (
    Ray Tracing)
45
46 k1 = 2*pi*n1/lambda;
47 k2 = 2*pi*n2/lambda;
48 k3 = 2*pi*n3/lambda;
49 k2x = cos(Theta_2) * 2*pi*n2/lambda;
50 k2y = sin(Theta_2) * 2*pi*n2/lambda;
51
52 % Reflection and Transmission Coefficients (Saleh Teich p. 210)
53 rs12 = ( eta_n2*sec(Theta_2) - eta_n1*sec(Theta_1) ) / ( eta_n2*
    sec(Theta_2) + eta_n1*sec(Theta_1) );

```

```

54 rp12 = ( eta_n2*cos(Theta_2) - eta_n1*cos(Theta_1) ) / ( eta_n2*
    cos(Theta_2) + eta_n1*cos(Theta_1) );
55 ts12 = 1 + rs12;
56 tp12 = (1 + rp12)*cos(Theta_1)/cos(Theta_2);
57
58 rs21 = ( eta_n1*sec(Theta_1) - eta_n2*sec(Theta_2) ) / ( eta_n1*
    sec(Theta_1) + eta_n2*sec(Theta_2) );
59 rp21 = ( eta_n1*cos(Theta_1) - eta_n2*cos(Theta_2) ) / ( eta_n1*
    cos(Theta_1) + eta_n2*cos(Theta_2) );
60
61 rs23 = ( eta_n3*sec(Theta_3) - eta_n2*sec(Theta_2) ) / ( eta_n3*
    sec(Theta_3) + eta_n2*sec(Theta_2) );
62 rp23 = ( eta_n3*cos(Theta_3) - eta_n2*cos(Theta_2) ) / ( eta_n3*
    cos(Theta_3) + eta_n2*cos(Theta_2) );
63
64 x_values = 0:dx:Lx;
65 x_values_reverse_label = Lx:-dx:0;
66 y_values = 0:dy:Ly;
67
68 NX = length(x_values);
69 NY = length(y_values);
70
71
72 %% Field Calculations – TE, s-Polarization
73
74 % Field Initialization
75 Es2_x(1:NX, 1:NY) = 0;

```

```

76 Es2_y(1:NX, 1:NY) = 0;
77 Es2_z(1:NX, 1:NY) = 0;
78
79 % General Rightward (m EVEN, x+) – ONLY Z COMPONENT (Ex,Ey = 0).
80 for m = 0:2:m_max
81     for x_index = 1:NX
82         for y_index = 1:NY
83             Es2_z(x_index, y_index) = Es2_z(x_index, y_index) + ...
84             +ts12*rs23^(m/2)*rs21^(m/2) *...
85             exp( 1i*k2x*(x_values(x_index) ) ) *...
86             exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
87             exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
88         end
89     end
90 end
91
92 % General Leftward (m ODD, x-) – ONLY Z COMPONENT (Ex,Ey = 0).
93 if ( m_max > 0 )
94     for m = 1:2:m_max
95         for x_index = 1:NX
96             for y_index = 1:NY
97                 Es2_z(x_index, y_index) = Es2_z(x_index, y_index) + ...
98                 +ts12*rs23^(m/2 + 0.5)*rs21^(m/2 - 0.5) *...
99                 exp( 1i*k2x*(Lx - x_values(x_index) ) ) *...
100                 exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
101                 exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
102             end

```

```

103 end
104 end
105 end
106
107 % Intensity Calculation (modulus squared)
108 Intensitys2(1:NX, 1:NY) = 0;    % Speeds up matlab by avoiding
    memory reallocations
109 for x_index = 1:NX
110 for y_index = 1:NY
111 Intensitys2(x_index, y_index) = ...
112 Es2_x(x_index, y_index) * conj( Es2_x(x_index, y_index) ) + ...
113 Es2_y(x_index, y_index) * conj( Es2_y(x_index, y_index) ) + ...
114 Es2_z(x_index, y_index) * conj( Es2_z(x_index, y_index) ) ;
115
116 Intensitys2(x_index, y_index) = real(n2)*real( Intensitys2(
    x_index, y_index) );
117 % Remove rounding complex errors
118 % Multiple by Re{n2}
119 end
120 end
121
122 % Calculations: Free Spectral Range, Visiblity Contrast
123 MIN_s_value = 1000;
124 MIN_s_index = 0;
125 MAX_s_value = 0;
126 MAX_s_index = 0;

```



```

127 for index_count = 1:round(( lambda/2/real(n2) / cos(Theta_2) )
    / dx)
128 if ( MIN_s_value > Intensitys2(index_count, 1) )
129 MIN_s_value = Intensitys2(index_count, 1);
130 MIN_s_index = index_count;
131 end
132 if ( MAX_s_value < Intensitys2(index_count, 1) )
133 MAX_s_value = Intensitys2(index_count, 1);
134 MAX_s_index = index_count;
135 end
136 end
137
138 FSR_s = abs( 2*( x_values(MAX_s_index) - x_values(MIN_s_index)
    ) );
139 % Should equal lambda/2/Re{n2}/cos(theta_2)
140
141
142 %% Field Calculations – TM, p-Polarization
143
144 % Field Initialization
145 Ep2_x(1:NX, 1:NY) = 0;
146 Ep2_y(1:NX, 1:NY) = 0;
147 Ep2_z(1:NX, 1:NY) = 0;
148
149 % General Rightward (m EVEN, x+) – (Ez = 0).
150 for m = 0:2:m_max
151 for x_index = 1:NX

```

```

152 for y_index = 1:NY
153   Ep2_x(x_index, y_index) = Ep2_x(x_index, y_index) + ...
154   -tp12*rp23^(m/2)*rp21^(m/2)*sin(Theta_2) *...
155   exp( 1i*k2x*(x_values(x_index) ) ) *...
156   exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
157   exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
158
159   Ep2_y(x_index, y_index) = Ep2_y(x_index, y_index) + ...
160   +tp12*rp23^(m/2)*rp21^(m/2)*cos(Theta_2) *...
161   exp( 1i*k2x*(x_values(x_index) ) ) *...
162   exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
163   exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
164 end
165 end
166 end
167
168 % General Leftward (m ODD, x-) - (Ez = 0).
169 if ( m_max > 0 )
170   for m = 1:2:m_max
171     for x_index = 1:NX
172       for y_index = 1:NY
173         Ep2_x(x_index, y_index) = Ep2_x(x_index, y_index) + ...
174         +tp12*rp23^(m/2+0.5)*rp21^(m/2-0.5)*sin(Theta_2) *...
175         exp( 1i*k2x*(Lx - x_values(x_index) ) ) *...
176         exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
177         exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
178

```

```

179 Ep2_y(x_index , y_index) = Ep2_y(x_index , y_index) + ...
180 +tp12*rp23^(m/2+0.5)*rp21^(m/2-0.5)*cos(Theta_2) *...
181 exp( 1i*k2x*(Lx - x_values(x_index) ) ) *...
182 exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
183 exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
184 end
185 end
186 end
187 end
188
189 % Intensity Calculation (modulus squared)
190 Intensityp2(1:NX, 1:NY) = 0;
191 for x_index = 1:NX
192 for y_index = 1:NY
193 Intensityp2(x_index , y_index) = ...
194 Ep2_x(x_index , y_index) * conj( Ep2_x(x_index , y_index) ) + ...
195 Ep2_y(x_index , y_index) * conj( Ep2_y(x_index , y_index) ) + ...
196 Ep2_z(x_index , y_index) * conj( Ep2_z(x_index , y_index) ) ;
197
198 Intensityp2(x_index , y_index) = real(n2)*real( Intensityp2(
    x_index , y_index) );
199 % Remove rounding complex errors
200 % Multiple by Re{n2}
201 end
202 end
203
204 % Calculations: Free Spectral Range, Visiblity Contrast

```

```

205 MIN_p_value = 1000;
206 MIN_p_index = 0;
207 MAX_p_value = 0;
208 MAX_p_index = 0;
209 for index_count = 1:round(( lambda/2/real(n2) / cos(Theta_2) )
    / dx)
210 if ( MIN_p_value > Intensityp2(index_count , 1) )
211 MIN_p_value = Intensityp2(index_count , 1);
212 MIN_p_index = index_count;
213 end
214 if ( MAX_p_value < Intensityp2(index_count , 1) )
215 MAX_p_value = Intensityp2(index_count , 1);
216 MAX_p_index = index_count;
217 end
218 end
219
220 FSR_p = abs( 2*( x_values(MAX_p_index) - x_values(MIN_p_index)
    ) );
221 % Should equal lambda/2/Re{n2}/cos(theta_2)
222
223
224 %% PLOTS
225
226 % Intensity - Linear Plot (y = 0)
227 figure(01)
228 clf
229 box on;

```

```

230 set(gca, 'fontsize', 14, 'FontName', 'Times New Roman')
231 plot(x_values_reverse_label, Intensitys2(1:end, 1), '-blue',
      x_values_reverse_label, Intensityp2(1:end, 1), '-red')
232 xlabel('Vertical Displacement, j [\mum]')
233 temp_ylabel = ylabel('Intensity');
234 set(temp_ylabel, 'position', get(temp_ylabel, 'position')-[Lx
      /25,0,0]);
235 axis([x_values(1) x_values(end) 0 2.4]);
236 %legend({'TE (s)', 'TM (p)'});
237
238 %
239 %% Intensity - 2D plot - TE Polarization (s)
240 % figure(02)
241 % clf
242 %
243 % subplot(1, 2, 1)
244 % [C,h] = contourf(x_values, y_values, Intensitys2.', 50);
245 % set(h, 'LineColor', 'none');
246 % caxis([0, real(n2)]);
247 % colorbar;
248 % axis([x_values(1) x_values(end) y_values(1) y_values(end)]);
249 % xlabel('x [\mum]')
250 % temp_ylabel = ylabel('y [\mum]', 'rot', 0);
251 % set(temp_ylabel, 'position', get(temp_ylabel, 'position')-[Lx
      /10,0,0]);
252 % daspect([1 1 1]);
253 % title('TE Polarization (s)');

```

```

254 %
255 % subplot(1, 2, 2)
256 % [C,h] = contourf(x_values, y_values, Intensityp2.', 50);
257 % set(h, 'LineColor', 'none');
258 % caxis([0, real(n2)]);
259 % colorbar;
260 % axis([x_values(1) x_values(end) y_values(1) y_values(end)]);
261 % xlabel('x [\mu m]')
262 % temp_ylabel = ylabel('y [\mu m]', 'rot', 0);
263 % set(temp_ylabel, 'position', get(temp_ylabel, 'position') - [Lx
    /10, 0, 0]);
264 % daspect([1 1 1]);
265 % title('TM Polarization (p)');
266 %
267 % ha = axes('Position', [0 0 1 1], 'Xlim', [0 1], 'Ylim', [0 1], 'Box
    ', 'off', 'Visible', 'off', 'Units', 'normalized', 'clipping', '
    off');
268 % text(0.5, 1, {'INTENSITY vs. 2D POSITION'; ...
269 %     ['Thickness = ', num2str(Lx, 3), ' \mu m, n_1 = ', num2str(
    n1), ', n_2 = ', num2str(n2), ', n_3 = ', num2str(n3), ...
270 %     ', \theta_1 = ', num2str(Theta_1_deg, 3), '^o, \theta_2 =
    ', num2str(Theta_2_deg, 3), '^o', ...
271 %     ', Wavelength = ', num2str(lambda), ' nm, FSR = ', num2str
    (lambda/2/real(n2)/cos(Theta_2), 3), ' \mu m']; '}', '
    HorizontalAlignment', 'center', 'VerticalAlignment', 'top')

```

A.2 Visibility variation with angle

```

1
2 % Title: FPI_02_VIS_vs_lambda_Plotter
3 % Author: Moez Haque
4 % Date Created: November 29, 2016
5 % Description: Outputs spatial intensity profile within a Fabry
    Perot for
6 %                TE and TM polarizations.
7
8 clear
9 clc
10
11 %% User Input
12 Theta_1_deg_MIN = 0;
13 Theta_1_deg_MAX = 89;
14 Theta_1_deg_step = 1;
15
16 Lx = 1;                % FPI wafer thickness, Microns
17 Ly = 1;                % Transverse length, Microns
18
19 lambda = 0.515;        % Free Space Wavelength, Microns
20 m_max = 10;            % Number of FPI pass orders to add
21
22 n1 = 1;                % Refractive Index, Medium 1
23 n2 = 1.46;             % Refractive Index, Medium 2 (complex
    allowed)
24 n3 = 4.22 + 0.038i;    % Refractive Index, Medium 3

```

```

25
26 mu_r_1 = 1;           % Relative Permeability , Medium 1
27 mu_r_2 = 1;           % Relative Permeability , Medium 2
28 mu_r_3 = 1;           % Relative Permeability , Medium 3
29
30 dx = 0.001;           % Discrete Space Step , Microns
31 dy = 2;               % Discrete Space Step , Microns
32
33
34 %% Loop Calculator
35
36 Critical_Angle_n1_n2 = asin( real(n1)/real(n2) ) / pi * 180;
37 Critical_Angle_n3_n2 = asin( real(n3)/real(n2) ) / pi * 180;
38
39 theta_1_values_deg = Theta_1_deg_MIN:Theta_1_deg_step:
    Theta_1_deg_MAX;
40 NTheta = length(theta_1_values_deg);
41
42 for theta_index = 1:1:NTheta
43     Theta_1_deg = theta_1_values_deg(theta_index);
44
45
46
47 % Pre-Calculations
48
49 %               Theta_1_deg = 40;   % Wave vector incident
    angle , degrees

```



```

50
51 epsilon_0 = 8.8541878176*10^(-12); % Permittivity of free space
52 mu_0 = 1.25663706 * 10^(-6);      % Permeability of free space
53
54 eta_n1 = sqrt( mu_r_1^2 * mu_0 / n1^2 / epsilon_0 ); %
    Impedence
55 eta_n2 = sqrt( mu_r_2^2 * mu_0 / n2^2 / epsilon_0 ); %
    Impedence
56 eta_n3 = sqrt( mu_r_3^2 * mu_0 / n3^2 / epsilon_0 ); %
    Impedence
57
58 Theta_1 = Theta_1_deg / 180 * pi;      % Propagation angle ,
    medium 1
59 Theta_2 = asin( n1*sin(Theta_1)/n2 ); % Propagation angle ,
    medium 2
60 Theta_2_deg = Theta_2 / pi * 180;      % Propagation angle ,
    medium 2
61 Theta_3 = asin( n2*sin(Theta_2)/n3 ); % Propagation angle ,
    medium 3
62 Theta_3_deg = Theta_3 / pi * 180;      % Propagation angle ,
    medium 3
63
64 Dy = Lx*tan(Theta_2); % y-axis displacement from each pass (
    Ray Tracing)
65
66 k1 = 2*pi*n1/lambda;
67 k2 = 2*pi*n2/lambda;

```

```

68 k3 = 2*pi*n3/lambda;
69 k2x = cos(Theta_2) * 2*pi*n2/lambda;
70 k2y = sin(Theta_2) * 2*pi*n2/lambda;
71
72 % Reflection and Transmission Coefficients (Saleh Teich p. 210)
73 rs12 = ( eta_n2*sec(Theta_2) - eta_n1*sec(Theta_1) ) / ( eta_n2*
    sec(Theta_2) + eta_n1*sec(Theta_1) );
74 rp12 = ( eta_n2*cos(Theta_2) - eta_n1*cos(Theta_1) ) / ( eta_n2*
    cos(Theta_2) + eta_n1*cos(Theta_1) );
75 ts12 = 1 + rs12;
76 tp12 = (1 + rp12)*cos(Theta_1)/cos(Theta_2);
77
78 rs21 = ( eta_n1*sec(Theta_1) - eta_n2*sec(Theta_2) ) / ( eta_n1*
    sec(Theta_1) + eta_n2*sec(Theta_2) );
79 rp21 = ( eta_n1*cos(Theta_1) - eta_n2*cos(Theta_2) ) / ( eta_n1*
    cos(Theta_1) + eta_n2*cos(Theta_2) );
80
81 rs23 = ( eta_n3*sec(Theta_3) - eta_n2*sec(Theta_2) ) / ( eta_n3*
    sec(Theta_3) + eta_n2*sec(Theta_2) );
82 rp23 = ( eta_n3*cos(Theta_3) - eta_n2*cos(Theta_2) ) / ( eta_n3*
    cos(Theta_3) + eta_n2*cos(Theta_2) );
83
84 x_values = 0:dx:Lx;
85 y_values = 0:dy:Ly;
86
87 NX = length(x_values);
88 NY = length(y_values);

```

```

89
90
91
92 %% Field Calculations – TE, s-Polarization
93
94 % Field Initialization
95 Es2_x(1:NX, 1:NY) = 0;
96 Es2_y(1:NX, 1:NY) = 0;
97 Es2_z(1:NX, 1:NY) = 0;
98
99 % General Rightward (m EVEN, x+) – ONLY Z COMPONENT (Ex,Ey = 0).
100 for m = 0:2:m_max
101     for x_index = 1:NX
102         for y_index = 1:NY
103             Es2_z(x_index, y_index) = Es2_z(x_index, y_index) + ...
104             +ts12*rs23^(m/2)*rs21^(m/2) *...
105             exp( 1i*k2x*(x_values(x_index)          ) ) *...
106             exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
107             exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
108         end
109     end
110 end
111
112 % General Leftward (m ODD, x-) – ONLY Z COMPONENT (Ex,Ey = 0).
113 if ( m_max > 0 )
114     for m = 1:2:m_max
115         for x_index = 1:NX

```

```

116 for y_index = 1:NY
117   Es2_z(x_index, y_index) = Es2_z(x_index, y_index) + ...
118   +ts12*rs23^(m/2 + 0.5)*rs21^(m/2 - 0.5) *...
119   exp( 1i*k2x*(Lx - x_values(x_index)) ) *...
120   exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
121   exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
122 end
123 end
124 end
125 end
126
127 % Intensity Calculation (modulus squared)
128 Intensitys2(1:NX, 1:NY) = 0;
129 for x_index = 1:NX
130   for y_index = 1:NY
131     Intensitys2(x_index, y_index) = ...
132     Es2_x(x_index, y_index) * conj( Es2_x(x_index, y_index) ) + ...
133     Es2_y(x_index, y_index) * conj( Es2_y(x_index, y_index) ) + ...
134     Es2_z(x_index, y_index) * conj( Es2_z(x_index, y_index) );
135
136     Intensitys2(x_index, y_index) = real(n2)*real( Intensitys2(
137         x_index, y_index) );
138
139 % Remove rounding complex errors
140 % Multiple by Re{n2}
141 end
142 end

```

```

142 % Calculations: Free Spectral Range, Visiblity Contrast
143 MIN_s_value = 1000;
144 MIN_s_index = 0;
145 MAX_s_value = 0;
146 MAX_s_index = 0;
147 for index_count = 1:round(( lambda/2/real(n2) / cos(Theta_2) )
    / dx)
148 if ( MIN_s_value > Intensitys2(index_count, 1) )
149 MIN_s_value = Intensitys2(index_count, 1);
150 MIN_s_index = index_count;
151 end
152 if ( MAX_s_value < Intensitys2(index_count, 1) )
153 MAX_s_value = Intensitys2(index_count, 1);
154 MAX_s_index = index_count;
155 end
156 end
157
158 FSR_s = abs( 2*( x_values(MAX_s_index) - x_values(MIN_s_index)
    ) );
159 % Should equal lambda/2/Re{n2}/cos(theta_2)
160
161
162 %% Field Calculations – TM, p-Polarization
163
164 % Field Initialization
165 Ep2_x(1:NX, 1:NY) = 0;
166 Ep2_y(1:NX, 1:NY) = 0;

```

```

167 Ep2_z(1:NX, 1:NY) = 0;
168
169 % General Rightward (m EVEN, x+) - (Ez = 0).
170 for m = 0:2:m_max
171     for x_index = 1:NX
172         for y_index = 1:NY
173             Ep2_x(x_index, y_index) = Ep2_x(x_index, y_index) + ...
174             -tp12*rp23^(m/2)*rp21^(m/2)*sin(Theta_2) *...
175             exp( 1i*k2x*(x_values(x_index)          ) ) *...
176             exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
177             exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
178
179             Ep2_y(x_index, y_index) = Ep2_y(x_index, y_index) + ...
180             +tp12*rp23^(m/2)*rp21^(m/2)*cos(Theta_2) *...
181             exp( 1i*k2x*(x_values(x_index)          ) ) *...
182             exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
183             exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
184         end
185     end
186 end
187
188 % General Leftward (m ODD, x-) - (Ez = 0).
189 if ( m_max > 0 )
190     for m = 1:2:m_max
191         for x_index = 1:NX
192             for y_index = 1:NY
193                 Ep2_x(x_index, y_index) = Ep2_x(x_index, y_index) + ...

```

```

194 +tp12*rp23^(m/2+0.5)*rp21^(m/2-0.5)*sin(Theta_2) *...
195 exp( 1i*k2x*(Lx - x_values(x_index) ) ) *...
196 exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
197 exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
198
199 Ep2_y(x_index, y_index) = Ep2_y(x_index, y_index) + ...
200 +tp12*rp23^(m/2+0.5)*rp21^(m/2-0.5)*cos(Theta_2) *...
201 exp( 1i*k2x*(Lx - x_values(x_index) ) ) *...
202 exp( 1i*k2y*(y_values(y_index) - m*Dy) ) *...
203 exp( 1i*k2*m*sqrt(Lx.^2+Dy^2) );
204 end
205 end
206 end
207 end
208
209 % Intensity Calculation (modulus squared)
210 Intensityp2(1:NX, 1:NY) = 0;
211 for x_index = 1:NX
212 for y_index = 1:NY
213 Intensityp2(x_index, y_index) = ...
214 Ep2_x(x_index, y_index) * conj( Ep2_x(x_index, y_index) ) + ...
215 Ep2_y(x_index, y_index) * conj( Ep2_y(x_index, y_index) ) + ...
216 Ep2_z(x_index, y_index) * conj( Ep2_z(x_index, y_index) );
217
218 Intensityp2(x_index, y_index) = real(n2)*real( Intensityp2(
    x_index, y_index) );
219 % Remove rounding complex errors

```

```

220 % Multiple by Re{n2}
221 end
222 end
223
224 % Calculations: Free Spectral Range, Visiblity Contrast
225 MIN_p_value = 1000;
226 MIN_p_index = 0;
227 MAX_p_value = 0;
228 MAX_p_index = 0;
229 for index_count = 1:round(( lambda/2/real(n2) / cos(Theta_2) )
    / dx)
230 if ( MIN_p_value > Intensityp2(index_count , 1) )
231 MIN_p_value = Intensityp2(index_count , 1);
232 MIN_p_index = index_count;
233 end
234 if ( MAX_p_value < Intensityp2(index_count , 1) )
235 MAX_p_value = Intensityp2(index_count , 1);
236 MAX_p_index = index_count;
237 end
238 end
239
240 FSR_p = abs( 2*( x_values(MAX_p_index) - x_values(MIN_p_index)
    ) );
241 % Should equal lambda/2/Re{n2}/cos(theta_2)
242
243
244 % Visibility calculator

```



```

245 MIN_Intensity_s(theta_index) = min(Intensitys2(:));
246 MAX_Intensity_s(theta_index) = max(Intensitys2(:));
247
248 MIN_Intensity_p(theta_index) = min(Intensityp2(:));
249 MAX_Intensity_p(theta_index) = max(Intensityp2(:));
250
251 end
252
253
254 Visibility_s = (MAX_Intensity_s - MIN_Intensity_s) ./ (
    MAX_Intensity_s + MIN_Intensity_s);
255 Visibility_p = (MAX_Intensity_p - MIN_Intensity_p) ./ (
    MAX_Intensity_p + MIN_Intensity_p);
256
257
258 %% Plots
259
260 % Min/Max Intensity vs. Angle
261 figure(03)
262 clf
263 hold on;
264
265 plot(theta_1_values_deg, MAX_Intensity_s, '-blue')
266 plot(theta_1_values_deg, MIN_Intensity_s, '--blue')
267 plot(theta_1_values_deg, MAX_Intensity_p, '-red')
268 plot(theta_1_values_deg, MIN_Intensity_p, '--red')
269 xlabel('\theta_1 [degrees]')

```

```

270 temp_ylabel = ylabel({'Normalized'; 'Intensity'; '(I = n2*E.E)'
    }, 'rot', 0);
271 set(temp_ylabel, 'position', get(temp_ylabel, 'position') - [(
    Theta_1_deg_MAX - Theta_1_deg_MIN)/30, 0, 0]);
272 axis([Theta_1_deg_MIN Theta_1_deg_MAX 0 2]);
273 title({'Intensity vs Input Angle (\theta_1)'; ...
274     ['Thickness = ', num2str(Lx), ' \mu m, n_1 = ', num2str(
        n1), ', n_2 = ', num2str(n2), ', n_3 = ', num2str(n3)
        , ...
275     ', Wavelength = ', num2str(lambda), ' nm']});
276 legend({'TE (s) - Max Intensity', 'TE (s) - Min Intensity', 'TM
    (p) - Max Intensity', 'TM (p) - Min Intensity'});
277
278 % Min/Max Intensity vs. Angle
279 figure(04)
280 clf
281 clf
282 hold on;
283 box on;
284 set(gca, 'fontsize', 12, 'FontName', 'Times New Roman')
285 plot(theta_1_values_deg, Visibility_s, '—blue', 'Linewidth', 2)
286 plot(theta_1_values_deg, Visibility_p, '—red', 'Linewidth', 2)
287 xlabel('Incident angle \theta_1 \circ')
288 ylabel('Visibility')
289 set(gca, 'XTick', sort([65, get(gca, 'XTick')]));
290 %temp_ylabel = ylabel({'Visibility'; '=(I_{max}-I_{min}) / (I_{
    max}+I_{min})'}, 'rot', 0);

```

```

291 %set(temp_ylabel, 'position', get(temp_ylabel, 'position') - [(
    Theta_1_deg_MAX - Theta_1_deg_MIN)/15,0,0]);
292 title({'Visibility vs Input Angle (\theta_1)'; ...
293       ['Thickness = ', num2str(Lx), ' \mu m, n_1 = ', num2str(
        n1), ', n_2 = ', num2str(n2), ', n_3 = ', num2str(n3)
        , ...
294       ', Wavelength = ', num2str(lambda), ' \mu m']})
295 legend({'TE (s)', 'TM (p)'}, 'Position', [0.2 0.15 0.1 0.2]);
296 legend boxoff;
297 axis([Theta_1_deg_MIN Theta_1_deg_MAX 0 1]);

```

Bibliography

- [1] D. M. Roper, S. Ho, M. Haque, and P. R. Herman, “Control of femtosecond laser interference ejection with angle and polarisation,” *Proc. SPIE*, vol. 10094, pp. 100940T–100940T–9, 2017.
- [2] S. Ho, M. Domke, D. M. Roper, H. Huber, and P. R. Herman, “Femtosecond laser quantized structuring in thin SiO_2 film,” *In Lasers and Electro-Optics (CLEO), 2016 Conference on - IEEE*, 2016.
- [3] C. Jeppesen, R. B. Nielsen, A. Boltasseva, S. Xiao, N. A. Mortensen, and A. Kristensen, “Thin film ag superlens towards lab-on-a-chip integration,” *Optics Express*, vol. 17, no. 25, pp. 22543–22552, 2005.
- [4] M. Focke, D. Kosse, C. Mullerm, H. Reinecke, R. Zengerle, and F. von Stetten, “Lab-on-a-foil: microfluidics on thin and flexible films,” *Lab on a Chip*, vol. 10, pp. 1365–1386, 2010.
- [5] S. Trolier-McKinstry and P. Muralt, “Thin film piezoelectrics for mems,” *Journal of Electroceramics*, vol. 12, no. 1, pp. 7–17, 2004.
- [6] G. Urban, G. Jobst, F. Kohl, A. Jachimowicz, F. Olcaytug, O. Tilado, P. Goiser, G. Nauer, F. Pittner, T. Schalkhammer, and E. Mann-Buxbaum, “Miniaturized thin-film biosensors using covalently immobilized glucose oxidase,” *Biosensors and Bioelectronics*, vol. 6, no. 7, pp. 555–562, 1991.

- [7] W. L. Murphy, T. C. McDevitt, and A. J. Engler, “Materials as stem cell regulators,” *Nature Materials*, vol. 13, pp. 547–557, 2014.
- [8] D. Chanda, L. E. Abolghasemi, M. Haque, M. L. Ng, and P. R. Herman, “Multi-level diffractive optics for single laser exposure fabrication of telecom-band diamond-like 3-dimensional photonic crystals,” *Optics Express*, vol. 16, no. 20, pp. 15402–15414, 2008.
- [9] S. Jeon, V. Malyarchuk, J. Rogers, and G. Wiederricht, “Fabricating three dimensional nanostructures using two photon lithography in a single exposure step,” *Optics Express*, vol. 14, no. 6, pp. 2300–2308, 2006.
- [10] M. Y. Xu, J. Li, L. D. Lilge, and P. R. Herman, “F2- laser patterning of indium tin oxide (ito) thin film on glass substrate,” *Applied Physics*, 2006.
- [11] V. Dinca, M. Farsari, D. Kafetzopoulos, A. Popescu, M. Dinescu, and C. Fotakis, “Patterning parameters for biomolecules microarrays constructed with nanosecond and femtosecond uv lasers,” *Thin Solid Films*, vol. 516, no. 18, pp. 6504–6511, 2008.
- [12] D. B. Chrisey, A. Pique, R. A. McGill, J. S. Horwitz, and B. R. Ringeisen, “Laser deposition of polymer and biomaterial films,” *Chemical Reviews*, pp. 553–576, 2003.
- [13] J. Grant-Jacob, B. Mills, M. Feinaeugle, C. L. Sones, G. Oosterhuis, M. B. Hoppenbrouwers, and R. W. Eason, “Micron-scale copper wires printed using femtosecond laser-induced forward transfer with automated donor replenishment,” *Optical Materials Express*, vol. 3, no. 6, pp. 747–754, 2013.
- [14] J. P. McDonald, V. R. Mistry, K. E. Ray, and S. M. Yalisove, “Femtosecond pulsed laser direct write production of nano- and microfluidic channels,” *Applied Physics Letters*, 2006.

- [15] J. P. McDonald, A. A. McClelland, Y. N. Picard, and S. M. Yalisove, “Role of a native oxide on femtosecond laser interaction with silicon (100) near the damage threshold,” *Applied Physics Letters*, vol. 86, 2005.
- [16] Y. Hosokawa, “Femtosecond multistep laser etching of transparent amorphous organic film,” *Japan Society of Applied Physics*, vol. 40, 2001.
- [17] K. Kumar, K. K. Lee, J. Nogami, J. Li, N. P. Kherani, and P. R. Herman, “Quantized structuring of transparent films with femtosecond laser interference,” *Light Science and Applications*, vol. 3, 2014.
- [18] K. Kumar, J. N. K. K. Lee, and P. R. Herman, “Interferometric laser processing,” *US20160158886 A1*, 2014.
- [19] Ho, “Interferometric femtosecond laser processing for nanostructuring inside thin film,” *Advance Optics Technology*, 2014.
- [20] S. Kuper and M. Stuke, “Ablation of polytetrafluoroethylene (teflon) with femtosecond uv excimer laser pulses,” *Applied Physics Letters*, vol. 54, p. 2, 1988.
- [21] K. M. Davis, K. Miura, N. Sugimoto, and K. Hirao, “Writing waveguides in glass with a femtosecond laser,” *Optics Letters*, vol. 21, no. 21, 1996.
- [22] L. Shah, A. Y. Arai, S. M. Eaton, and P. R. Herman, “Waveguide writing in fused silica with a femtosecond fiber laser at 522 nm and 1 mhz repetition rate,” *Optics Express*, vol. 13, no. 6, pp. 1999–2006, 2005.
- [23] A. Dragomir, D. N. Nikogosyan, K. A. Zagorulko, P. G. Kryukov, and E. M. Dianov, “Inscription of fiber bragg gratings by ultraviolet femtosecond radiation,” *Optics Letters*, vol. 28, no. 22, pp. 2171–2173, 2003.
- [24] A. Martinez, M. Dubov, I. Khrushchev, and I. Bennion, “Direct writing of fibre bragg gratings by femtosecond laser,” *Electronics Letters*, vol. 40, no. 19, 2004.

- [25] A. M. Streltsov and N. F. Borrelli, “Fabrication and analysis of a directional coupler written in glass by nanojoule femtosecond laser pulses,” *Optics Letters*, vol. 26, no. 1, pp. 42–43, 2001.
- [26] R. R. Gattass and E. Mazur, “Femtosecond laser micromachining in transparent materials,” *Nature Photonics*, vol. 2, pp. 219–225, 2008.
- [27] J. F. Dusing, T. Eichele, J. Koch, O. Suttmann, and L. Overmeyer, “Laser surface processing of integrated thin film systems on arbitrarily shaped components,” *Procedia Technology*, vol. 15, pp. 122–128, 2014.
- [28] C. Kerse, H. Kalaycioglu, P. Elahi, B. Certin, D. K. Kesim, O. Alkcaalan, S. Yavas, M. D. Asik, B. Oktem, K. Hoogland, R. Holzwarth, and F. O. Idlay, “Ablation-cooled material removal with ultrafast bursts of pulses,” *Nature*, vol. 537, pp. 84–88, 2016.
- [29] J. W. Hutchinson and Z. Suo, “Mixed mode cracking in layered materials,” *Advances in Applied Mechanics*, vol. 29, no. 3, p. 63, 1992.
- [30] J. A. Thornton and J. E. Greene, “Sputter deposition processes,” *Handbook of Deposition Technologies for Films and Coatings- Science, Technology and Applications, Second Eddition*, William Andrew Publishing/ Noyes, 1994.
- [31] Z. Suo and J. W. Hutchinson, “Interface crack between two elastic layers,” *International Journal of Fracture*, vol. 43, pp. 1–18, 1990.
- [32] J. S. Wang and A. G. Evans, “Effects of strain cycling on buckling, cracking and spalling of a thermally grown alumina on a nickel-based bond coat,” *Acta Materialia*, vol. 47, no. 2, 1999.
- [33] T. Li and Z. Suo, “Ductility of thin metal films on polymer substrates modulated by

- interfacial adhesion,” *International Journal of Solids and Structures*, vol. 44, no. 6, pp. 1696–1705, 2007.
- [34] R. P. Berkelaar, P. Bampoulis, E. Dietrich, H. P. Jansen, X. Zhang, E. S. Kooij, D. Lohse, and H. J. W. Zandvliet, “Water-induced blister formation in a thin film polymer,” *Langmuir*, vol. 31, no. 3, pp. 1017–1025, 2015.
- [35] J. R. Serrano and D. G. Cahill, “Micron-scale buckling of SiO_2 on Si,” *Journal of Applied Physics*, vol. 92, 2002.
- [36] J. R. Serrano and D. G. Cahill, “Laser-induced blistering of thin SiO_2 on Si,” *Microscale Thermophysical Engineering*, vol. 9, no. 2, pp. 155–164, 2005.
- [37] J. Bohandy, B. F. Kim, and F. J. Adrian, “Metal deposition from a supported metal film using an excimer laser,” *Journal of Applied Physics*, vol. 60, 1986.
- [38] J. Bohandy, B. F. Kim, F. J. Adrian, and A. N. Jette, “Metal deposition from a supported metal film using an excimer laser,” *Journal of Applied Physics*, vol. 63, 1988.
- [39] M. Chatzipetrou, G. Tsenkenis, V. Tsouti, S. Chatzandroulis, and I. Zergioti, “Biosensors by means of the laser induced forward transfer technique,” *Applied Surface Science*, vol. 278, pp. 250–254, 2013.
- [40] A. K. Nguyen and R. J. Narayan, “Liquid-phase laser induced forward transfer for complex organic inks and tissue engineering,” *Annals of Biomedical Engineering*, vol. 45, pp. 84–99, 2017.
- [41] Y. Deng, P. Renaud, Z. Guo, Z. Huang, and Y. Chen, “Single cell isolation process with laser induced forward transfer,” *Journal of Biological Engineering*, vol. 11, 2017.

- [42] S. Ho, P. Jha, and P. R. Herman, “Quantized blistering of transparent films with femtosecond laser interference,” *Photonics West*, 2016.
- [43] A. D. Rakic, “Algorithm for the determination of intrinsic optical constants of metal films: application to aluminum,” *Applied Optics*, vol. 34, pp. 4755–4767, 1995.
- [44] I. H. Malitson and M. J. Dodge, “Refractive index and birefringence of synthetic sapphire,” *Optical Society of America*, vol. 62, p. 1405, 1972.
- [45] D. E. Zelmon, D. L. Small, and D. Jundt, “Infrared corrected sellmeier coefficients for congruently grown lithium niobate and 5 mol.oxide-doped lithium niobate,” *Optical Society of America*, vol. 14, pp. 3319–3322, 1997.
- [46] I. H. Malitson, “Interspecimen comparison of the refractive index of fused silica,” *Optical Society of America*, vol. 55, pp. 1205–1208, 1965.
- [47] M. A. Green and M. J. Keevers, “Optical properties of intrinsic silicon at 300k,” *Progress in Photovoltaics*, vol. 3, no. 3, pp. 189–192, 1995.
- [48] K. Luke, Y. Okawachia, M. R. E. Lamont, A. L. Gaete, and M. Lipson, “Broadband mid-infrared frequency comb generation in a Si_3N_4 microresonator,” *Optics Letters*, vol. 55, pp. 1205–1208, 1965.
- [49] S. M. Eaton, *Contrasts in Thermal Diffusion and Heat Accumulation Effects in the Fabrication of Waveguides in Glasses using a Variable Repetition Rate Femtosecond Laser*. PhD thesis, University of Toronto, 2008.
- [50] K. J. Vahala, “Optical microcavities,” *Nature*, vol. 424, pp. 839–846, 2003.
- [51] M. R. Foreman, J. D. Swaim, and F. Vollmer, “Whispering gallery mode sensors,” *Advances in Optics and Photonics*, vol. 7, no. 2, pp. 168–240, 2015.
- [52] H. Hora, “Nonlinear confining and deconfining forces associated with the interaction of laser radiation with plasma,” *Physics of Fluids*, vol. 12, no. 189, 1969.

- [53] K. J. Edwards and A. D. Rutenberg, “Microbial response to surface microtopography: the role of metabolism in localized mineral dissolution,” *Chemical Geology*, vol. 180, pp. 19–32, 2001.