Investigations into femtosecond laser hybrid manufacturing for 3D power sources

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**INVESTIGATIONS INTO
FEMTOSECOND LASER HYBRID
MANUFACTURING FOR 3D
POWER SOURCES**

THAM, NICHOLAS CHENG YANG

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2020

**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare that it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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A/P Murukeshan V. M.

Authorship Attribution Statement

This thesis contains material from two (2) paper(s) published/communicated in the following peer-reviewed journal(s) and one (1) patent filed/accepted in the following country(s) in which I am listed as an author.

Contents from Chapters 4 and 5 are published as **Tham N.C.Y.**, P.K. Sahoo, Y. Kim, C. Hegde, S.W. Lee, Y.-J. Kim, V.M. Murukeshan, *Thermally controlled in-situ formation of localised porous graphene for integrated graphene-paper electronics*. Advanced Materials Technologies, 2021. 6 (5): p. 2001156.

And as a related patent as **Tham, N.C.Y.**, P.K. Sahoo, V.M. Murukeshan, Y.-J Kim and M.J. Low, *A Methods And An Apparatus For Manufacturing A Porous Graphene Layer Across A Precursor Material Layer On A Substrate Through Thermally Localised Laser Graphitisation*, Singapore Application No. 10202010197X, Patent pending.

The contributions of the co-authors are as follows:

- I, together with Dr. P. K. Sahoo and Assoc. Prof. V. M. Murukeshan conceived the initial idea and designed the experiments.
- I performed instrumentation, sample fabrication and characterisation by Raman spectroscopy, XPS, confocal microscopy for the samples.
- Mr. C. Hegde performed FESEM characterisation and analysis.
- I, together with Dr. P. K. Sahoo co-developed and coded the analytical temperature model.
- Dr. Y. Kim performed the characterisation of the MSCs and MBs.
- Asst. Prof. S. W. Lee and Dr. Y. A. Kim performed analysis of the MSC and MB results.
- I performed the characterisation of the humidity sensors.
- I, together with Dr. P. K. Sahoo, wrote the initial manuscript draft. The manuscript was revised by all authors. Assoc. Prof. V. M. Murukeshan and Asst. Prof. Y. -J. Kim supervised the research and corrected the manuscript. All authors reviewed and approved the final manuscript.
- This work was done when Dr. P. K. Sahoo and Asst. Prof. Y. -J. Kim were in Nanyang Technological University.

Contents from Chapter 6 are published as **Tham, N.C.Y.**, P.K. Sahoo, Y.-J. Kim, V.M Murukeshan, *Ultrafast volume holography for stretchable photonic structures*. Optics Express, 2019. **27**(9); p. 12196-12212.

The contributions of the co-authors are as follows:

- I, together with Dr. P. K. Sahoo, Asst. Prof. Y. -J. Kim and Assoc. Prof. V. M. Murukeshan conceived the initial idea and designed the experiments.
- I performed instrumentation and sample fabrication.
- Dr. P. K. Sahoo developed and analysed the finite-difference time-domain (FDTD) simulations.
- I, together with Dr. P. K. Sahoo performed all of the characterisation and other experiments.
- I, together with Dr. P. K. Sahoo wrote the initial manuscript draft. Assoc. Prof V. M. Murukeshan and Asst. Prof. Y. -J. Kim supervised the research and corrected the manuscript. All authors reviewed and approved the final manuscript.
- This work was done when Dr. P. K. Sahoo and Asst. Prof. Y. -J. Kim were in Nanyang Technological University.

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A handwritten signature in blue ink, consisting of a stylized 'N' followed by a horizontal line and a small loop.

Nicholas Tham Cheng Yang

13th January 2021

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Abstract

The changing energy needs of a new generation of smart wearables and Internet-of-Things (IoT) devices present a growing challenge that cannot be met by existing technologies. These small and compact devices come with tight form factors and energy requirements demanding higher performance and site-specific energy sources such as micro-batteries (MB) and micro-supercapacitors (MSCs). Current MBs and MSCs, however, do not yet meet these energy requirements. The 2D design of these power sources limits either the amount of energy stored (energy capacity) or the rate of energy release (power capacity). Surpassing these limitations require moving beyond these 2D designs, made possible by exploiting the third dimension. Compared to 2D MBs and MSCs, a combination of high power and energy capacities for MBs and MSCs can be achieved with 3D structures. However, the fabrication of 3D structures for MBs and MSCs faces major challenges. Existing fabrication strategies, which include 3D structures formed through template-less nanostructure growth or in-situ material deposition are still limited by high costs and complexity. Therefore, there is a definite need for cost-effective and scalable alternatives to fabrication.

Two such alternatives are femtosecond direct laser writing (fsDLW) and femtosecond laser interference lithography (fsLIL). fsDLW is an umbrella term where femtosecond (10^{-15} s) laser pulses are focused and scanned across a material surface to alter, deposit, or otherwise remove material through unique laser-material interaction phenomena. These phenomena allow for unprecedented control over in-situ material manipulation to form unique 3D features at different scales. One of these 3D features is randomly arranged 3D porous graphene (PG) flakes. PG can be formed directly from fsDLW in a single step, eliminating costs associated with multiple process steps. fsDLW PG therefore vastly simplifies the fabrication of high-performance 3D MSCs and MBs. fsLIL, in contrast, is a patterning process where femtosecond pulses interfere to form a variety of regular periodic interference pattern to pattern different materials. One area of research in this thesis is the direct patterning of optically transparent substrate materials such as PDMS with fsLIL. High aspect ratio structures can thus be formed directly in the bulk of optically transparent materials, enabling high aspect ratio 3D micro-batteries without the need for complex and expensive photolithographic steps. Therefore, this thesis will explore how high energy and power density 3D MB and MSC structures could be fabricated using fsDLW and fsLIL. These developments are supported by in-depth analysis of formation mechanisms and material characterisation for 3D MBs and MSCs.

The first major contribution of the research work presented in this thesis is the research and development of instrumentation, methodologies, and set-ups to achieve better stability and control over fsDLW and fsLIL. Improvements in femtosecond laser stability are first achieved

through the in-line monitoring of femtosecond laser pulses, such as pulse repetition rate, fluence and number of pulses during fabrication, reducing the impact of laser fluctuations and drift on fsDLW and fsLIL. These improvements then form the foundation for development of a fsDLW methodology to uniformly fabricate PG. This methodology consists of three key steps. First, in the design phase, acceleration and deceleration ‘wings’ are added to designs to reduce the impact of uneven fluence from mechanical movement of the galvano-scanner mirrors. Next, during the sample preparation phase, a temporary adhesive layer is developed to minimise any curling or warping of precursor materials during fsDLW. Lastly during the set-up preparation phase, a method to repeatably control sample height is developed. Through these three key steps, uniform and repeatable PG is demonstrated. The yield and repeatability of PG fabrication is thus improved, minimising the influence of unwanted factors during fabrication. This methodology is demonstrated with a custom lab-built fsDLW platform consisting of a femtosecond laser source coupled with in-line monitoring and a two axis galvano-scanner. A fsLIL platform incorporating the same in-line monitoring is developed in parallel. Strict design considerations due to the low temporal coherence of femtosecond pulses and the requirement for high fluence patterning are considered. From these design considerations, a two beam fsLIL platform is developed for low angle ($< 10^\circ$) large pitch ($> 1 \mu\text{m}$) periodic patterning in 1D. This set-up includes the development of a method to quickly calibrate the fsLIL set-up for patterning. By doing so, optical path difference (OPD) is kept within the coherence length of the femtosecond pulses for patterning. Together, these improvements in instrumentation, methodology and set-up enable consistent, repeatable, and controlled fsDLW and fsLIL, which is critical for any deeper research.

Predicting the formation of PG from fsDLW is critical to optimise PG for use in 3D power sources. Therefore, the next step in this investigation is the modelling of femtosecond laser-material interaction to predict PG formation. An analytical temperature model is developed to predict the temperature rise induced by impinging femtosecond pulses in a material’s cross-section. This model considers laser parameters and changing material properties with temperature. Predicting PG formation is achieved from a predefined top surface boundary temperature ($T_{grphn} = 1775 \text{ K}$) taken to be the minimum temperature required for PG formation. The temperature model is experimentally validated by comparing the predicted formation of PG with actual PG formation with the fsDLW platform and methodology discussed previously. Material changes in irradiated regions are identified through Raman spectroscopic analysis and optical characterisation. Experimental validation reveals that the analytical model can accurately predict and function as a proxy for the formation of PG above 1775 K. Subsequently, these optimised PG structures are demonstrated in 3D MBs. The performance of PG as an active anode for 3D MB is then characterised and analysed. An initial

energy capacity of $0.37 \text{ mA h cm}^{-2}$ is observed at 2°C discharge rate, and even at 17°C , up to $0.03 \text{ mA h cm}^{-2}$ is still maintained for 1000 cycles at close to 100% Coulombic efficiency. These results showcase the potential for PG formed from fsDLW in 3D MBs. The model developed in this research work lays the groundwork for a subsequent exploration into in-situ integration of MSCs with fsDLW and PG.

Integrating site-specific 3D power sources into thermally sensitive materials such as paper becomes possible using the same temperature model. With some minor improvements, the same model can be used to predict the temperature rise at both the top and bottom surfaces of PI tape. A thermally localised laser graphitisation (LLG) regime can then be identified to achieve in-situ PG integration. Parameters for LLG are determined from the model by first predefining a lower boundary for thermal damage at this bottom surface (348 K) in combination with the same surface boundary temperature (1775 K). With these parameters, localised PG (LPG) from PI can be fabricated in-situ without causing damage to the electronics substrate below from excessive heating. Thermochromic paper, which changes colour above a defined temperature is used to validate the model. LLG is critical to integrate site-specific power sources into thermally sensitive electronics. LPG MSCs are demonstrated and characterised on paper together with other useful LPG sensors for humidity. LPG MSCs demonstrate high capacitive performance, with 0.428 mF cm^{-2} at scan rates of 10 mV s^{-1} , and even an increase in scan rates to $10,000 \text{ mV s}^{-1}$ only reduces performance by two-thirds, falling in line with reported PG MSCs. LPG humidity sensors are found to repeatably detect humidity across a range of 4.2% to 7.64% for up to three cycles, with a maximum deviation of $\sigma = 0.64$. Together, these results demonstrate LPG's usefulness for high performance, self-powered graphene paper electronics.

Lastly, the bulk structuring of optically transparent materials through fsLIL for 3D MBs and MSCs is studied. The investigation also targeted towards the fabrication of 3D structures within such materials. The potential ability of these structures is demonstrated for alternate applications in optics. To demonstrate these alternatives 3D volume phase gratings are holographically patterned in unmodified optically transparent polydimethylsiloxane (PDMS). The previously discussed fsLIL platform and methodology is used to form Δn of 1.95×10^{-4} in unmodified PDMS with $1 \mu\text{m}$ periodicity across a thickness of $180 \mu\text{m}$. These VPGs are then demonstrated as active beam steering units and tuneable spectroscopic optical elements. Results from this research work will be critical for further research into the direct patterning of substrate materials for 3D power sources.

The major findings, original contributions and future work proposed in this thesis are envisaged to contribute towards the cost-effective and scalable fabrication of high performance and high-capacity 3D power sources for the next generation of smart wearable devices.

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List of Symbols

Symbol	Description
V	Amount of voltage
I	Amount of current
q	Amount of charge
t	Time
Q	Total energy capacity of a power source
I_{ch}	Charging current
I_{dis}	Output or discharge current
P	Total power capacity of a power source
C	Total capacitance of a micro-supercapacitor
ϵ	Electrical permittivity of a material
A	Area of capacitive surface
d	Distance between capacitive surfaces
ϵ	Electromotive force, or emf
ϵ_{net}	Net electromotive force, or emf. Difference between the reduction potentials of both half-cells and is therefore the force driving the current to do work in a battery
Li^+	Positive lithium ion
e^-	Free electron
V_{supply}	Supply voltage
I_{cap}	Current across capacitor
V_{cap}	Voltage across capacitor
ν_0	Central frequency of femtosecond pulse wavefunction
$E(t)$	Electric field strength varying in time
$A(t)$	Envelope function containing the electric strength variation
ω_0	Central angular frequency
Φ_0	Femtosecond pulse phase
τ_p	Femtosecond pulse duration
$I(t)$	Temporal intensity function
ϵ_0	Electrical permittivity of vacuum
c	Speed of light
n	Refractive index of material
ω_0	Gaussian beam waist or focus
$\Phi(t)$	Temporal phase term

$\Phi_a(t)$	Time-dependent phase function
$\omega(\quad)$	Momentary or instantaneous light frequency
λ	Wavelength
E	Energy
h	Planck's constant
N	Number of photons
W_{abs}	Absorbed energy density
A	Absorption coefficient
F	Pulse fluence
l_{abs}	Absorption depth in material
P_{peak}	Peak power of a laser pulse
E_p	Pulse energy
e	Exponent
ω	Gaussian beam width
P_{avg}	Average power of femtosecond beam
f	Repetition rate
I_{peak}	Pulse peak intensity
P_{peak}	Pulse peak power
F_{th}^N	Incubation dependent damage threshold
ξ	Metal incubation factor
F_{th}^1	Threshold fluence from one pulse
F_{th}^∞	Threshold fluence after infinite amount of pulses
k	Dielectric incubation factor
$F_p(x, y)$	Fluence distribution of individual pulses across a rastered area
F_{peak}	Peak fluence of single pulse
x	x-(horizontal) direction
y	y-(vertical) direction
ω_{theo}	Theoretical Gaussian beam width
ω_{eff}	Actual feature width formed in material
$I_t(r)$	Time-independent intensity distribution of any arbitrary periodic pattern
I	Intensity
E	Amplitude
$\hat{e}$	Polarisation vector
$\mathbf{k}$	Wavevector
ϕ	Phase

δ	Phase difference between two interfering beams
I_0	Intensity of each interference beam (assuming equal intensity)
V_{ij}	Contrast term between beam pair i and j
τ_c	Interference coherence time
L_c	Interference coherence length
$\Delta\nu$	Optical bandwidth of laser
E_{loss}	Pulse energy loss in optical element
E_T	Total pulse energy
E_R	Reflected pulse energy
E_{UR}	Un-reflected pulse energy
.dxf	2D vector file format
.jpeg	Image file format
.png	Image file format
v	Galvano-scanner scanning speed
D	Thermal diffusivity
$T(\vec{r}, t)$	Rate of change of temperature distribution
$f(\vec{r}, t)$	Rate of change of heating
α	Absorption length
ρ	Material density
C_p	Heat capacity
$Q_{laser}(\vec{r}, t)$	Rate of change of generated heat density
R	Reflectance
z	Z direction
r	Radial distance from centre of focal spot
$\delta(t)$	Dirac delta function
ω_0	Gaussian beam waist diameter
$T_1(r, z, t)$	Temperature distribution due to one pulse in r and z directions
T_{peak}	Peak temperature rise
τ	Rate of heat diffusion
$T_z(r, t)$	Temperature distribution at position z
erfc	Complementary error function
κ	Thermal conductivity
T	Total temperature rise
T_{accum}	Accumulated temperature due to multiple pulses
t_L	Pulse period

T_1	Temperature rise due to of one pulse
T_{amb}	Ambient temperature
$H(t - nt_L)$	Heaviside function to only consider pulses that have reached at time t
T_{top}	Temperature at top surface
T_{grphn}	Graphitisation temperature
R_s	Sheet resistance
T_{btm}	Temperaure at bottom surface
T_{dmg}	Substrate damage temperature
I_D	Intensity of Raman spectrum D peak
I_G	Intensity of Raman spectrum G peak
I_{2D}	Intensity of Raman spectrum 2D peak
L_a	Graphene crystallite size
sp^2	Hybrid molecular orbital of one s and two p orbitals
sp^3	Hybrid molecular orbital of one s and three p orbitals
C_A	Areal capacitance
V_1, V_2	Potential window during CV measurement
Δn	Refractive index modulation
Λ	Periodicity
n_o	Refractive index of material
n_{min}	Minimum refractive index
n_{max}	Maximum refractive index
t	Volume phase grating thickness
θ_B	Bragg angle
η	Diffraction efficiency
w	Width of unit cell of constant refractive index
t_R	Width of right unit cell with cosine square modulation
t_L	Width of left unit cell with cosine square modulation
dc	Duty cycle analogue where $dc = w/(t_L + w + t_R)$
Subscript	
dis	Discharge
ch	Charge
cap	Capacitive
p	Pulse
abs	Absorption
avg	Average

<i>th</i>	Threshold
<i>tho</i>	Theoretical
<i>eff</i>	Actual or effective
<i>c</i>	Coherence
<i>accum</i>	Accumulative
<i>L</i>	Length
<i>amb</i>	Ambient
<i>grphtn</i>	Graphitisation
<i>s</i>	Sheet
<i>btm</i>	Bottom
<i>dmg</i>	Damage
<i>a</i>	Crystallite area
<i>A</i>	Area
<i>B</i>	Bragg
<i>R</i>	Right
<i>L</i>	Left

List of Abbreviations

Abbreviation	Explanation
a-C	Amorphous carbon
A	Amorphous
AAO	Anodic aluminum oxide
ACF	Activated carbon fibre
AEF	Area enlargement factor
AFP	Accumulated fluence profile
AM	Additive manufacturing
ALD	Atomic layer deposition
BET	Brunauer–Emmett–Teller
C	Carbonisation
CC	Current collector
CPA	Chirped pulse amplification
CV	Cyclic voltammetry
CVD	Chemical vapour deposition
CW	Continuous wave
DIC	Differential interference contrast

DLW	Direct laser writing
DMT	Double microtube
DPSS	Diode-pumped solid state
ED	Electrodeposition
EDB	Economic Development Board
EMIMBF4	1-ethyl-3-methylimidazolium tetrafluoroborate electrolyte
ELT	Extended low temperature
FE	Finite element
FESEM	Field emission scanning electron microscope
FDM	Fused deposition modelling
FDTD	Finite-difference time-domain
fsDLW	Femtosecond direct laser writing
fsLIL	Femtosecond laser interference lithography
FWHM	Full-wave-at-half-maximum
G	Graphitisation
GCD	Galvanostatic charge-discharge
GCPL	Galvanostatic cycling with potential limitation
GO	Graphene oxide
HOMO	Highest occupied molecular orbital
HRTEM	High resolution transmission electron microscope
HT	High temperature
IoT	Internet of Things
IPP	Industrial Postgraduate Programme
IR	Infrared
LbL	Layer-by-layer
LATP	Lithium aluminium titanium phosphate
LCO	Lithium cobalt oxide
LED	Light emitting diode
LFP	Lithium iron phosphate
LIB	Lithium-ion battery
LIFT	Laser induced forward transfer
LIL	Laser interference lithography
LIG	Laser induced graphene
LIPON	Nitrogen-doped lithium phosphate
LIPSS	Laser induced periodic surface structures
LLG	Thermally localised laser graphitisation

LMO	Lithium manganese oxide
LPG	Localised porous graphene
LT	Low temperature
LTO	Lithium titanium oxide
LUMO	Lowest unoccupied molecular orbital
MB	Micro-battery
MP	Micropillars
MSC	Micro-supercapacitor
OPD	Optical path difference
PDMS	Polydimethylsiloxane
PFSAP	Panasonic Factory Solutions Asia Pacific
PG	Porous graphene
PI	Polyimide
PLD	Pulsed layer deposition
PML	Perfectly matched layer
PVD	Physical vapour deposition
RH	Relative humidity
RIE	Reactive ion etching
rGO	Reduced graphene oxide
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
SMT	Simple microtubes
SMU	Source-measure unit
THG	Third harmonic generated
TPP	Two-photon polymerisation
UV	Ultraviolet
VIS	Visible
VPG	Volume phase grating
XPS	X-ray photoelectron spectroscopy

Chapter 1: Introduction

This chapter begins with a discussion on the background and motivation. This discussion leads to the development of the research problem statement. A brief review of the limitations of existing 2D micro-batteries (MBs) and micro-supercapacitors (MSCs) follows. The major research objectives and scope are identified and presented. The chapter concludes with a brief discussion on the organisation of the thesis.

1.1 Background and motivation

Smart wearables and Internet-of-Things (IoT) devices are the latest bid to bring technology into every facet of our lives. During this fourth industrial revolution aptly labelled “Industry 4.0”. smartwatches, e-skin sensors, e-textiles and even smart home devices are but a few examples of an ever-expanding range of devices around us [1]. These devices aim to help consumers connect not only with others through integrated social networks but with their own ailments, moods, and needs. Smart wearables and IoT devices are becoming more compact and conformal, to become embedded in the environment in close proximity to consumers [2]. These new form factors result in site-specific electrical power supply and storage needs that cannot be easily met by existing power sources [3]. To solve this issue, the on-chip integration of power sources is critical.

New energy storage technologies have sprung up to meet those requirements. Micro-batteries (MBs) and micro-supercapacitors (MSCs) are two such complementary miniaturised technologies, designed to fulfil the site-specific needs of smart wearable technologies [4]. MBs generally meant for long-term energy storage, with larger energy capacities (1 mW h cm^{-2}) with steady, if comparatively lower power capacities ($< 5 \text{ mW cm}^{-2}$) to power devices over a longer period. Reversible lithium-ion chemistry generally forms the basis of electrochemical storage in MBs. Lithium-ion chemistries have the greatest energy density out of all other established secondary (rechargeable) battery systems [5]. In contrast, charge storage in MSCs is based on the combination of electrostatic absorption and desorption of capacitive ions in carbon-based electrodes or electrochemical pseudo capacitance arising from rapid redox reactions in pseudocapacitive materials without any chemical changes to the electrodes [6]. These allow MSCs to handle many large spikes in power consumption due to high power density ($> 10 \text{ mW cm}^{-2}$) However, this performance comes at a cost of a much lower energy capacity ($< 0.1 \text{ mW cm}^{-2}$). These power sources, unlike more familiar large cylindrical cells, are not only small and

compact but in some cases are also flexible and even stretchable so that the power needs can be met by on-chip integration [7].

1.1.1 3D vs 2D power sources – increased energy density through the third dimension

Contemporary MBs and MSCs are generally made of either thin *planar* (2D) films of active materials stacked together on the scale of one to tens of μm or thick planar films on the order of hundreds of μm thick, both with a 2D footprint smaller than 10 mm^2 (**Figure 1.1**) [3, 5]. Despite differences in energy storage mechanisms, both 2D MBs and MSCs contain *active* (i.e. contributes to energy storage performance) materials that consist of two electrode layers sandwiching an electrolyte layer. These layers are then combined with a current collector and sealed in protective packaging to form thin film or thick film 2D MBs and MSCs.

Figure 1.1. Schematic representation of thin film micro-batteries (MB) and micro-supercapacitors (MSCs). Active layers that contribute to the electrochemical and capacitive performance of thin film MBs and MSCs respectively are the electrolyte and electrodes. The substrate, current collector and packaging/barrier layers are considered inactive and non-contributing.

However, limitations in energy capacity restrict the application of contemporary 2D thick and thin film MBs to smart wearables and IoT devices. Currently reported and commercially available thin film MBs and MSCs are only suitable for low-to-medium powered applications, such as smaller Internet of Things (IoT) sensors, implantable medical devices and smart cards, with power requirements in the range of $1 - 10\text{ mA h}$ [1, 5, 6, 8]). While thin and therefore potentially smaller than coin or pouch cells of a similar footprint, thin film MB and MSC energy capacity is limited by the amount of active material in a fixed footprint area, resulting in limited energy capacity (mA h) [3, 9]. The main limiting factor for 2D thin film MBs and MSCs, therefore, is energy capacity. Thick film MBs and MSCs are limited in the opposite manner, with greater energy capacities, but poor power capacities that are unable to provide enough energy at large enough currents [10]. Based on these established technologies, the only option to increase energy capacity while still maintaining faster charging and discharging capabilities would be to increase the *active surface area* of the thin film MB and MSC for the *same footprint*

so that energy capacity can scale accordingly [9]. However, device size and tight form factors severely limit available space for scaling. Therefore, energy capacity remains limited for thin film MBs and MSCs, especially if constrained to small wearable devices. New strategies would therefore have to be adopted to develop a new generation of MBs and MSCs capable of powering the next generation of high-red devices.

To tackle these energy and power limitations, researchers have looked towards exploiting the third dimension, to maximise the available surface area for lithium-ion transfer in MBs and capacitive charge storage in MSCs for the same available footprint (**Figure 1.2**). The addition of 3D structures to MBs and MSCs would be able to greatly increase the active surface area (and therefore areal energy density) for the same amount of packaging and substrate material.

Figure 1.2. Advantages of 3D MBs and MSCs over thick and thin film 2D MBs and MSCs. Adapted from [11] with permission from IOP Publishing.

1.1.2 Fabricating 3D power sources – 3D MBs and 3D MSCs

Many different strategies have been demonstrated with respect to the fabrication of 3D structures that would support the required increase in power and energy capacity ranging in complexity, available surface area, and cost. Four broad strategies are currently in use today that are widely applicable to both MBs and MSCs: micro-machined or etched silicon substrates to create 3D structures on which MB and MSC materials are later deposited, or various methods to form complex templates of 3D structures before material deposition, template-less growth of nanostructures, and the direct deposition of active materials into 3D structures via additive manufacturing (also known as 3D printing) [3, 12-20].

However, several limitations restrict the wider application of these strategies. For example, micro-machined or etched Si substrates requires multiple micro-machining and/or photolithographic steps, which adds to process complexity and cost before deposition of active layers can even occur. Furthermore, the Si substrate contributes to the inactive volume of the power source, reducing the performance of the power source [12]. Templating strategies in comparison, require additional masking and template removal steps, which may cause contamination of the active materials deposited after. Current template-free strategies focus on the growth of nanostructured current collectors and active materials, which itself is a complex and costly process involving high (up to 480 °C) temperatures and pressures [21]. Finally, any discussion of 3D structure fabrication cannot exclude additive manufacturing (AM). AM, in contrast with traditional subtractive manufacturing, describes a group of technologies that share a few fundamental features: layer-by-layer construction of 3D structures with minimal waste and “free” complexity [20]. In additive manufacturing, materials are deposited only where needed, and energy is transferred to materials via heating, curing, sintering or melting to form 3D structures. Additive manufacturing research on 3D MBs and MSCs is currently focused on direct material deposition processes, where MB and MSC materials are directly printed into 3D structures (inkjet printing, laser deposition printing). However, complexities in maintaining (or even enhancing) the electrochemical properties of MB and MSC materials while developing suitable rheological properties for deposition limits wider application of direct deposition [22]. Further ex-situ (separate and external) post deposition heat treatment is also required, limiting the scalability of the process. All these limitations result in processes that are difficult to scale cost-effectively. Therefore, there is a need for alternative strategies to fabricate 3D structures for MBs and MSCs in a simple and scalable manner.

1.1.3 Femtosecond laser hybrid manufacturing – template-free 3D structuring

The fabrication of 3D structures with femtosecond lasers is one such alternative strategy. Compared to continuous wave (CW) lasers, femtosecond lasers emit photons in a series of *ultrashort* pulses with durations below 1 picosecond. These highly compressed pulses are able to transfer terawatts of peak power (P_{peak}) or more to deposit, remove or otherwise alter a material to form 3D MB and MSC structures [23]. These pulses can be manipulated and controlled in various ways to create different kinds of 3D structures. One of the methods is femtosecond direct laser writing (fsDLW). In combination with beam scanning optics, femtosecond pulses can be directed and focused via a series of scanning mirrors and lenses to manipulate material over a wide 2D area or even 3D volume by “writing” on the material itself [24]. Using fsDLW, single step, in-situ and template-free 3D structuring can be achieved in a

wide variety of ways. For example, fsDLW was used to structure the surface of thick films of active materials at both the micro- and nanometre scales [23, 25]. This multi-scaled structuring was found to greatly improve the performance of as-deposited materials. Most attractively for the direct integration of power sources into IoT devices, fsDLW can be used to directly create active material by physically or chemically altering inactive precursor materials.

The photoreduction of thin films of graphene oxide (GO) by fsDLW is one such method to form randomly arranged 3D porous graphene (PG) structures. These graphene structures have been demonstrated for use as high capacity (960 mA h g^{-1}) porous anodes for 3D MBs, without the need for additional current collectors [26, 27]. The carbonisation of polymers such as polyimide (PI) using fsDLW to form porous 3D networks of carbon-based materials is another such method [28]. Such PG structures are particularly suited to both MBs and MSCs, due to the excellent conductivity of graphene itself and large, active surface areas [29]. These 3D structures are also robust and can be integrated into wearables and IoT devices [7]. Another key advantage of directly forming such 3D structures is on-chip integration, such that MBs and MSCs can be directly fabricated on the devices themselves, rather than separately. With such a wide variety of methods to form 3D structures for MBs and MSCs, fsDLW, therefore, is an excellent candidate for further research and development.

For greater design control and flexibility close to the diffraction limit, femtosecond laser interference lithography (fsLIL) would be the preferred choice for fabricating 3D structures. From the superposition of two or more temporally coherent femtosecond pulses, fsLIL can form periodic intensity patterns with regions of high (crests) and low (troughs). These high and low-intensity regions can be used to pattern nanometre-scaled 3D structures for MB fabrication reproducibly and without the error often introduced by serial writing processes. A key demonstration of fsLIL (and LIL in general) was the fabrication of LIL-defined 3D MBs that exhibited impressive power capacities [30]. Instead of relying on multi-step photolithography, fsLIL could also be used to directly pattern MB and MSC substrate materials to further increase available surface area [31]. Patterning of MB and MSC substrate materials could then be done in-situ, integrating the substrate patterning process into the overall MB and MSC fabrication process.

Femtosecond lasers also are powerful complementary tools that enable *hybrid* manufacturing of 3D MBs and MSCs in addition to direct (additive) material deposition. When combined with materials deposition using in-situ deposition technologies like inkjet printing or robocasting, full MB or MSC device can then be fabricated, combining active 3D MB and MSC materials with inactive materials such as packaging and current collectors.

In summary, fsDLW and fsLIL are both simple, cost-effective, and scalable alternative to conventional strategies, enabling template-free and single-step fabrication of 3D MB and MSC structures.

1.2 Research Objective

Leveraging on the advantages of fsDLW and fsLIL and the identified research gap, the main objectives of this doctoral thesis include the research and development of femtosecond laser-based concepts and methods to fabricate 3D structures for realising high-performance 3D MBs and MSCs. These objectives are summarised as given below:

- (i) Investigations into femtosecond direct laser writing (fsDLW) to form active 3D micro-battery (MBs) and micro-supercapacitor (MSC) porous graphene (PG) structures directly onto devices for on-chip integration of power sources. These 3D structures are to have high electrical conductivity ($> 50 \Omega \text{ sq}^{-1}$) for 3D MBs and MSCs. The targeted energy capacity and capacitance of PG 3D MBs and MSCs are $0.15 \text{ mA h cm}^{-2}$ and 0.3 mF cm^{-2} and above respectively to improve upon the performance of reported 3D MBs and MSCs.
- (ii) Investigations into thermally localised laser graphitisation (LLG) using fsDLW. The localised PG (LPG) formed are to be demonstrated for integrated graphene-paper MSCs and electronics. LPG 3D MSCs should similarly demonstrate a capacitance exceeding 0.3 mF cm^{-2} scan rate to exceed the performance of reported 3D MSCs.
- (iii) Research and development of femtosecond laser interference lithography (fsLIL) system for direct patterning of different substrate materials to form 3D structures throughout the bulk with a minimum area enlargement factor (AEF) of 30.

The proposed research includes the development of novel concepts, relevant theoretical simulations, fabrication methodologies, and follow-up experimental validation.

1.3 Research Scope

To achieve the above-stated objectives, a significant amount of research work has to be done, which will be outlined in the research scope given below.

- (i) Research and development of a fsDLW methodology to enable repeatable and uniform fabrication of 3D PG structures from polyimide (PI).
- (ii) Theoretical modelling and experimental validation to predict PG formation from temperature rise in PI, incorporating femtosecond laser and material parameters.
- (iii) Investigations into the performance and characteristics of PG 3D MBs from PI.

These PG 3D MBs must exhibit an energy capacity exceeding $0.15 \text{ mA h cm}^{-2}$ to match the performance of other reported 3D MBs.

- (iv) Theoretical modelling and experimental validation of LPG formation from the developed LLG process. LPG formation is modelled from temperature rise across the cross-section of PI to enable in-situ integration of graphene electronics.
- (v) Investigations into the performance and characteristics of in-situ integrated LPG 3D MSCs from PI. LPG 3D MSCs must exhibit comparable performance to existing 3D MSCs, with a minimum areal capacitance of 0.3 mF cm^{-2} or higher.
- (vi) Research and development of a two-beam fsLIL set-up for direct interference patterning of 3D structures into substrate materials. The set-up must enable patterning of features with periodicities $> 1 \mu\text{m}$ while minimising the use of refractive optics to reduce overall energy loss.
- (vii) Direct interference patterning (fsLIL) of periodic structures in optically transparent substrate materials to fabricate 3D structures through the bulk of the material. The periodic structure should have a pitch of at least $1 \mu\text{m}$ across a thickness of at least $100 \mu\text{m}$, so that the 3D structure would eventually have an AEF of at least 30.

1.4 Organisation of the thesis

The thesis is organised into seven chapters, each of which discusses in greater detail the work completed towards fulfilling the objectives elucidated above, and the following steps to take after. A short paragraph summarises each chapter's contents at the beginning of each chapter.

The thesis begins in **Chapter 1**, where the background and motivations of the research work are presented.

Chapter 2 covers a literature review of current state-of-the-art research into the fabrication of 3D MBs and MSCs via conventional fabrication techniques and femtosecond laser-based techniques. Particular attention is given to the fundamentals of femtosecond laser-material interaction. Fabrication techniques are then benchmarked according to a set of quantitative criteria for cost-effective and scalable fabrication strategies. From this literature review, fsDLW and fsLIL are firmly established as alternatives compared to conventional techniques, meeting the criteria for facile, cost-effective, and scalable fabrication strategies required for 3D power source fabrication through the comparative benchmarking.

Chapter 3 details the set-ups, methodologies and instrumentation developed for fsDLW and fsLIL to fabricate 3D structures for MBs and MSCs. The chapter begins with an in-line monitoring set-up for femtosecond laser parameters. A methodology to reliably and repeatably

fabricate 3D PG devices from a custom lab-built fsDLW set-up is described next, followed by the development of a fsLIL set-up for high fluence and large pitch periodic patterning with low temporal coherence pulses.

In **Chapter 4**, the development and validation of an analytical temperature model to predict the formation of PG from fsDLW from temperature rise is elaborated on. The chapter begins with a theoretical derivation of the temperature model from initial boundary conditions, followed by modelled temperature distribution at the top surface of the polyimide precursor material. From this model, PG is predicted to form above a temperature of 1775 K (T_{grphn}). These predictions are then experimentally validated through the fsDLW set-up and methodology discussed in Chapter 3. The results of the experimental validation and material characterisation of PG are discussed, which leads to in-depth analysis of the proposed formation mechanisms of PG from fsDLW. The chapter concludes with a demonstration and characterisation of PG formed from fsDLW as an anode in a lithium-ion MB half-cell.

In **Chapter 5**, the previously developed analytical temperature model is utilised to predict a set of fsDLW laser parameters for LLG to demonstrate the in-situ fabrication and integration of graphene and paper electronics. These laser parameters for LLG are experimentally validated with the same fsDLW set-up and methodology as before. These LLG parameters are shown to form LPG from PI adhered on without inducing damage to the substrate below. Analysis of these results along with material characterisation of the LPG formed is discussed in greater detail in the chapter. A demonstration with the characterisation of LPG MSCs and humidity sensors fabricated on paper concludes the chapter.

Chapter 6 focuses on the results obtained from direct 3D structuring of optically transparent substrates with fsLIL. Using the fsLIL set-up developed in **Chapter 3**, direct 3D material structuring is achieved in optically transparent PDMS. The structures formed, however, are not suitable for 3D power source fabrication at this stage. Instead, the chapter focuses on the use of these 3D structures as volume phase gratings (VPGs) for active beam steering and tunable spectroscopic applications. The fsLIL structuring process is discussed, followed by the results of structuring in PDMS films. An analysis and finite-difference time-domain (FDTD) simulation of the formation mechanisms is also discussed in detail. The chapter concludes with a demonstration of the VPGs for tuneable beam steering and spectroscopy.

Lastly, the thesis concludes in **Chapter 7**, where the main contributions made in the thesis are emphasised along with recommendations for future work.

The contents of this thesis are summarised in the research roadmap (**Figure 1.3**) presented in the next page.

Figure 1.3. Research roadmap summarising the different research tasks identified and completed. The roadmap compartmentalises major objectives of the thesis into smaller sub-objectives to structure the research systematically. Novel and adapted contributions are indicated.

Chapter 2: Literature Review – Fabricating 3D structures for micro-batteries (MBs) and micro-supercapacitors (MSCs)

Developing an understanding on current micro-battery (MB) and micro-supercapacitor (MSC) technologies and existing research gaps necessitates a thorough review of fundamental concepts, which leads to the chosen solution used to tackle these limitations through this chapter. The fundamental characteristics, working principles and complementary utility of MBs and MSCs are first covered, followed by a detailed discussion on the limitations of existing 2D power sources and how 3D power sources could tackle these limitations. A set of quantitative criteria are identified for cost-effective and scalable 3D power source fabrication. Conventional methods of fabricating 3D power sources are then reviewed, with a critical eye on the scalability and cost-effectiveness of these methods based on the developed criteria. Furthermore, femtosecond laser-based fabrication methods, which are promising alternatives to these conventional methods of fabrication are discussed in detail, followed by a review of key femtosecond laser parameters that are used to control the formation of 3D structures in different materials. The chapter concludes with the outcome of the literature review, highlighting the research gap in the challenges and limitations facing conventional methods of fabrication.

2.1 Fundamentals of micro-batteries (MBs) and micro-supercapacitors (MSCs)

Before beginning the discussion on the fabrication of micro-batteries (MBs) and micro-supercapacitors (MSCs) in greater detail, a firm understanding of the fundamental concepts of energy storage in MB and MSCs and how MBs and MSCs are used in smart wearables and IoT devices is required.

2.1.1 Key performance parameters – MBs and MSCs

The ability for MBs or MSCs to power any device is described by a few key performance parameters, namely the output voltage, energy capacity, capacitance, power capacity and cycle life. As power sources, MBs and MSCs play different but complementary roles. MBs are constant voltage sources, which provide a constant driving electrical force to do work in an

external circuit measured in volts (V). This driving force moves electrons around the external circuit, resulting in the flow of current (I), which is the movement of charge (q) per unit time (t). The total energy capacity of a battery is Q in amp-hours (A h), which is the total charge transferred by I_{ch} or I_{dis} on charging or discharging. Batteries with high capacities are more attractive, as devices can function longer. In batteries, Q is determined by the form and type of *active* materials used, which directly contribute to its energy capacity, measured in mA h g⁻¹, mA h L⁻¹ or energy capacity per area (mA h mm⁻²). The power capacity (P) (mW) or specific power (in mW g⁻¹, mW L⁻¹ or mW mm⁻²) of a battery, in contrast, is the loading capability, or ability to quickly (high power) or slowly (low power) release energy where $P = IV$.

MSCs in contrast, do not provide a constant voltage during discharge. Rather, MSCs are used to rapidly supply high peak currents when required. The ability for a capacitor to store charge is measured by the capacitance (C) of the MSC in farads (F), where $C = q/V$. Capacitance is also directly proportional to the available surface area across the active materials where $C = \epsilon A/d$, therefore a larger amount of energy can be stored with a greater active surface area. The amount of energy stored Q and power capacity P of the MSC is similarly measured in mA h and W.

Lastly, over multiple charging and discharging cycles, the capacity of MBs (which are generally rechargeable) and MSCs may degrade, due to unwanted side reactions between the electrodes and the electrolytes, or electrolyte evaporation in MSCs [32, 33]. The number of charge/discharge cycles before capacity retention falls below 80% is known as the cycle life. Since rechargeable batteries are often used in systems in which battery replacement is difficult if not possible, such as in smart wearable devices, long cycle life is essential for repeated charge/discharge cycles over a long operational life. In summary, these key performance parameters determine the overall ability for MBs and MSCs to effectively power any device. Next, to gain a better understanding of how to optimise these parameters, a more in-depth investigation into energy storage mechanisms in MBs and MSCs is required.

2.1.2 Energy storage in MBs

At its most basic level, a battery is made up of one or more electrochemical cells, which convert chemical energy into electrical energy to do work on an external circuit. MBs are based off this same fundamental concept, except with a massive reduction in size below 10 mm². Each cell is made up of two electrodes; a cathode, which is positively charged and an anode, which is negatively charged, and an electrolyte, which enables ion movement between the cathode and anode, without allowing electron (electrical) flow. Redox reactions take place at both the cathode and anode, which through the transfer of charges between materials, convert chemical

into electrical energy, and vice versa. Cells can be further divided into half-cells containing only an anode or a cathode, and each of these half-cells has an electromotive force (emf (ϵ)) corresponding to the reduction potentials of the electrode materials compared to a reference. The net emf (ϵ_{net}) of the cell is then the difference between the reduction potentials of both half-cells and, therefore, is the force driving the current to do work in an external circuit.

Figure 2.1. Schematic of lithiation and delithiation in rechargeable lithium-ion batteries. When a lithium-ion battery is discharged, Li^+ ions travel from the anode (graphite) to the cathode (LiCoO_2), and the reverse occurs when the battery is charged. The separator ensures that Li^+ ions can travel between the electrodes while no electrical contact is made between the two electrodes to prevent short-circuiting. Reproduced from [34] under the CC BY-NC-ND license from Elsevier.

Lithium-ion chemistries are the most common choice for MBs. because of the highest terminal voltages (3.30 – 3.70V) and capacities available compared to other battery types [5, 35]. MBs based on lithium-ion chemistries provide electrical energy through the reversible *intercalation* (or insertion) of positive lithium ions (Li^+) between anode and cathode. In a conventional lithium-ion cell (**Figure 2.1**), typically based off a graphite (C) anode, and lithium cobalt oxide (LiCoO_2) cathode, energy is discharged when the following redox reaction occurs at the anode (**Equation (2.1)**) [35]:

Li^+ ions then migrate from the anode through the electrolyte, intercalating through the cathode. The following redox reaction then occurs, where the Li^+ ions are integrated into the lithium cobalt oxide (**Equation (2.2)**):

In the outer circuit, electrons flow in the opposite direction to do work. This process is reversed, and the cell charged when an opposite voltage is applied across the cell terminals and the Li^+

ions are reversibly intercalated back into the anode [36]. The rate and amount of these reactions are strongly affected by the availability of active surface area, where a greater available surface area results in a larger volume of reactions being able to take place at the same time due to increased ionic diffusion through the electrolyte, i.e. a greater power capacity [37]. If the amount of active electrode material scales with the available surface area, more energy capacity is also possible [9].

These three materials make up the active materials of a MB. Any other material, including current collectors, which connect the battery to the external circuit, packaging, which protects the battery from the external environment (and vice versa) and binders, which in some formulations hold particles of active material together are considered *inactive*, even though they are essential to the overall functioning of the MB.

Unlike batteries, energy in capacitors is not stored and released through chemical reactions. Instead, capacitors store energy through electric fields. In a standard two plate capacitor, a dielectric material is placed between two electrodes, and electrical energy is stored through the electric field set up between the two plates when the capacitor is charge (q) through a source voltage (V). The capacitance (C) of a capacitor, therefore, is the ability for a capacitor to store charge.

Supercapacitors (also known as ultracapacitors) are a specific type of capacitor with much greater energy capacities in exchange for slower discharge rates and cycle lives [38]. Micro-supercapacitors (MSCs), like MBs, are simply the miniaturised variant of supercapacitors. Additional mechanisms within the supercapacitor, specifically storage of charge within a Helmholtz double-layer and through rapid redox reactions in pseudocapacitive materials allow for this greater energy capacity. Depending on the dominant mechanism, supercapacitors can therefore generally be classified as electric double-layer capacitors (EDLCs), pseudo capacitors or a hybrid of both [39]. Supercapacitors are like batteries in construction: the active components and materials of a supercapacitor consists of two electrodes (generally of the same material) and an electrolyte to facilitate ion transfer.

When EDLCs are charged, the surface of the electrodes where the electrolyte (often liquid) is in contact with form an electrical double-layer (**Figure 2.2(a)**). Whereas a single layer of charges on each plate would be formed on a simple two-plate capacitor, two layers of electrical charges are instead formed with opposite polarities, one at each surface of the electrodes, and the other within the electrolyte formed from mobile ions. Between these two layers, solvent molecules act as a dielectric, physically adsorbed onto the surface of the electrode to separate the two layers. No transfer of charge occurs throughout the formation of this double-layer, nor

are there any chemical changes to the electrode or electrolyte unlike in a battery. This double layer effectively acts as a second set of “plates” within the EDLC, therefore the standard capacitance formula applies, such that material with high surface area and extremely thin double-layers have very high capacitance [3].

Electric double-layers also form within pseudo capacitors. However, within the electric double-layer, mobile ions within the electrolyte that have a particular affinity to the electrode material can cross the double layer and adsorb onto the electrode surface. This mechanism results in pseudo capacitance, where energy is stored in the electrode surface through rapid faradaic redox reactions (**Figure 2.2(b)**). No chemical reaction takes place between the electrode and adsorbed ions; only a charge transfer occurs [40]. Because pseudo capacitance arises from redox reactions, these values are strongly determined by the chemical affinity between the electrode and electrolyte materials. Examples of strongly pseudocapacitive materials include transition metal oxides. The structure and availability of active surface area for adsorption also contributes in large part to pseudo-capacitance, to contribute to a larger energy capacity without the need for compromising power capacity.

Figure 2.2. Schematic of capacitive mechanisms in supercapacitors. (a) Rapid redox reactions at the surface of pseudocapacitive materials give rise to pseudo-capacitance (b) Charges stored in the electric double-layer formed at the liquid interface of the electrode and electrolyte give rise to double layer capacitance. Adapted from [40] with permission from the Royal Society of Chemistry.

Both the formation of the Helmholtz electric double-layer and pseudocapacitive redox reactions contribute to the increased energy capacity of the supercapacitor for energy storage. The formation of the electric double layer and pseudo capacitance is both rapid and unlimited in principle, translating to the impressively long cycle lives of real MSCs in general [38]. Like MBs, the construction of an MSC would not be complete without the addition of inactive materials, such as current collectors and packaging.

These energy storage mechanisms in MBs and MSCs allow both to play different, but complementary roles in power smart wearables and IoT devices. With this foundation, the complementary roles of MBs and MSCs in powering wearables can then be discussed in further detail.

2.1.3 Complementary energy sources – MBs and MSCs

Power needs in wearables and IoT devices generally fall into two categories: constant and long-term powering of circuit components such as processors and memory with relatively low current consumption, and large spikes in peak current consumption during the collection and communication of raw data to and from the device [41]. The needs for both categories can be generally met by MBs and MSCs, respectively.

Compared to MSCs, redox reactions in a lithium-ion MB occur at a much slower rate, resulting in a lower power density that is unable to meet spikes in peak current consumption consistently and reliably. (**Figure 2.3**). However, a greater amount of energy can be stored and released through these electrochemical reactions. More importantly, the voltage across the battery stays relatively constant throughout discharging (minus losses due to internal resistance) as net emf is based on the chemistry of the battery itself, which generally does not change during discharge. Importantly, energy capacity also strongly determined by the current draw rate or C-rate. With a lower C rate, more energy can be supplied by the MB overall. MBs are therefore the most appropriate for as a long-term, low current consumption source.

MSCs, in contrast, do not provide a constant voltage while discharging. Instead, the overall voltage is generally determined by the original supply voltage (V_s) used and amount of charge across the two electrodes. As current (I_{cap}) is discharged, the voltage across the capacitor (V_{cap}) will decrease, according to the relation $V_{cap} = V_s(1 - e^{(-t/RC)})$. However, because I_{cap} can be discharged rapidly, MSCs are useful to power spikes of peak current consumption (**Figure 2.3**). MBs would not even be able to achieve or would have to severely compromise on energy capacity to achieve such power densities at higher C-rates. The greater cycle life of MSCs also ensures that these spikes in requirements can be met for more reliable performance overall.

Both MBs and MSCs, therefore, play critical and complementary roles in power smart wearables and IoT devices. Further research in improving MBs and MSCs to better play these roles is therefore necessary.

Figure 2.3. Ragone plots of supercapacitors and batteries. Ragone plot depicting the characteristic times (specific energy over specific power) of supercapacitors and batteries respectively, as well as the overall direction of improvements in characteristic times. The eventual goal of battery and supercapacitor development is marked as the question mark in the plot. Reproduced from [42] with permission from Elsevier.

2.2 Types of MB and MSC structures

2.2.1 2D MB and MSC structures

Contemporary MBs and MSCs are generally constructed in 2D with thin or thick films. Thin film MB and MSCs are made up of several thin ($1 - 10 \mu\text{m}$) layers of materials which, depending on the design, can be stacked in multiple layers, or arranged in a single plane with interdigitated fingers between the two electrodes. For MBs, a current collector is first deposited on a substrate, and subsequent layers of the anode, electrolyte, cathode and second current collector in a sandwich configuration, before being tightly packaged together. In total, a thin film cell should have a thickness of less than $20 \mu\text{m}$ [5]. Thin film MSCs in contrast are generally constructed in an in-plane interdigitated design due to limitations in solid electrolytes available [3]. Both 2D MBs and MSCs utilise similar fabrication techniques, to deposit these thin films of active materials, such as atomic layer deposition (ALD), physical and chemical vapour deposition (PVD/CVD), sol-gel, electrodeposition (ED), pulsed laser deposition (PLD), layer-by-layer (LbL) assembly, and laser transfer printing techniques [27, 43-54]. Being 2D in nature, thin film MBs and MSCs have the advantage of higher power capacity, as the thin layers of material allows energy to be released quickly. Direct deposition of active materials in thin layer also reduces the need for inactive binders within the material (compared to thick film MBs and MSCs) effectively improving the specific capacity and power of thin film MBs and MSCs.

However, the main disadvantage of current thin film MBs and MSCs is the low energy capacity (<1 mA h for MBs) and capacitance (< 30 mF cm⁻²), arising from the limited by the amount of active material available for energy storage both in thickness (MBs) and in available surface area (MSCs) [3]. Conventional methods used with thick film MBs and MSCs to increase the amount of material and available surface area, such as post-deposition rolling or folding (into prismatic, cylindrical or pouch cells) are generally not suitable, due to the brittleness of the materials used in thin film materials. Directly increasing the thickness of the layers with thin film deposition methods is not viable either, as depositing increased layer thickness is slow (especially with ALD and LbL), increases the chances of cracks and other defects forming in layers which can contribute to self-discharge or short-circuiting, and reduces ion mobility and therefore the specific power of MBs in particular [5, 9]. While thin film MBs and MSCs may be able to meet some of the power consumption needs in wearables, limitations in energy capacity limit use higher energy consumption uses. Different strategies will have to be adopted to meet the needs of the next generation of smart wearable devices.

The thick film counterpart to thin film MBs and MSCs consist of much thicker layers (100 μ m) of active materials, forming cells of thicknesses from 50 to 1000 μ m [3, 5]. The larger amount of material results in much larger energy capacities for MBs and increased active surface area for MSCs. However, thick film MBs and MSCs come with the trade-off of lower power densities. owing to diffusion-limited ion mobility within thick electrode layers [5]. Thick film materials are prepared as particles (such as LCO for the cathode and graphite for the anode for MBs or transition metal and graphene dispersions for MSCs) suspended in polymer (or other) binders, forming thick porous films [19]. A liquid electrolyte is added to provide ionic pathways. Prepared materials are then deposited onto current collector sheets by a variety of methods, including screen printing, laser coating/printing, 3D printing, or inkjet printing [19, 20, 55-57]. While capacity could be further improved by folding or rolling post-deposition due to the mechanical stability afforded by the polymer binders, power capacity remains limited due to low ion and electron conductivities within the thick porous films [3]. Therefore, despite the increased capacity relative to thin film MBs and MSCs, thick film MBs and MSCs are also inadequate for meeting the power needs of smart wearables and IoT devices.

Figure 2.4. Schematic diagram of thin and thick film MBs. Thin film MBs generally do not contain significant amounts of inactive material between current collectors, resulting in total thicknesses below 20 μm . Thick film MBs conversely contain a large proportion of additives and binders along with the active material, resulting in a much thicker overall construction from 50 to 1000 μm . Both types of MB are constructed similarly in a layer-by-layer construction. Adapted from [5] with permission from the Royal Society of Chemistry.

2.2.2 3D MB and MSC structures

3D structures in MBs and MSCs bring together the advantages of both thin film (high power) and thick film (high capacity) in the same footprint. By having thin layers of active materials over a large 2D area, a short ionic current path can be maintained for high power density, while having a much larger amount of material (in surface area) to provide enhanced energy capacity. One measure of surface area increment for well-defined 3D structures is the Area Enlargement Factor (AEF), which is the ratio of the available electrode area of a 3D power source versus the 2D area of its footprint, i.e. $\text{AEF} = \text{Area}_{3D} / \text{Area}_{2D}$. As a design goal, an AEF of 30 is good, while an AEF of 50 is comparable to that of nanostructured materials [11, 58]. By increasing AEF, the percentage of “inactive” materials is reduced, resulting in a much higher total MB or MSC current obtained for similar internal current density [9]. For nanostructures or other randomly arranged 3D structures that cannot be easily measured by Brunauer–Emmett–Teller (BET) surface area analysis, increases in active surface area can be estimated by improvements in electrochemical performance instead versus a planar reference or through electrochemical surface area (ECSA) measurements [59].

3D structures can commonly be categorised as having “semi”-3D structures or “true” 3D structures [5]. Semi-3D structures have one or two 3D micro or nanostructured electrodes that

can be separated by a planar separator or interdigitated with a liquid/gel electrolyte separating the two to reduce ion path distances between electrodes. True 3D MBs and MSCs in comparison feature active and current collectors sequentially layered over a 3D structure such that the cell can be considered as “locally” 2D while “globally” 3D. These 3D structures are not limited to any particular size range, and can span the range of nanometres, with templated virus anodes to millimetres with additive manufacturing, depending on the method of fabrication [56, 60]. All of these, however, share the same characteristic of extending beyond the base 2D plane to expand the available surface area for energy storage.

The designs of both types of structures aim to achieve two key objectives: the first, is to reduce the mean ion path through the electrodes to the electrolyte, by increasing the active area of the electrodes [5]. Shortening ion diffusion distance, therefore, helps to improve power densities without sacrificing energy capacity or capacitance [3, 15]. This objective can be achieved in various ways; by directly increasing the porosity of electrode particles used, or using nanostructured materials, or depositing thin films of active materials over high AEF 3D structures [61-64]. These methods increase the amount of material and hence the available energy capacity or capacitance of the electrodes (up to 0.03 to 0.1 mW h cm⁻² for 3D MSCs [3]). The second objective of increasing ion conductivity across the electrolyte can be achieved either by choosing a thinner solid electrolyte, one with higher ion conductivity, or using a liquid/gel type electrolyte depending on the 3D structures fabricated. Therefore, by increasing the available surface area and ion conductivity, the available energy capacity and capacitance of 3D MBs and MSCs can be improved without a loss of power capacity.

2.2.3 Criteria for choosing a fabrication strategy

Four broad strategies that can be used to fabricate both 3D MBs and MSCs are currently under research today. The first and oldest strategy relies on the use of micro-machined or otherwise etched silicon substrates, to form the 3D structures on which current collectors and active MSC materials are later deposited. The second strategy involves the use of various templates, such as virus templates or anodic aluminium oxide (AAO) to build up 3D structures before the templates are either removed or deposited on. Template-free techniques involve the growth of various nanostructured active materials or current collectors on a substrate, and the most recent strategy involves the direct deposition of active materials into 3D structures via additive manufacturing technologies or laser deposition printing.

To effectively compare the strengths and limitations of each of these strategies, several key criteria have to be established and quantified. These criteria must capture the ability for a particular process to fabricate 3D structures for high-performance and capacity batteries, as

well as consider issues in process scalability and cost. From these requirements, and an extensive review of existing literature, five key criteria of a desirable fabrication strategy can be developed as follows in the next page.

- Formation of 3D structures that are actively involved in energy storage, thereby reducing the number of passive components, and improving the overall energy density of the device.
- Formation of 3D scalable features as possible to increase the available active surface area for energy storage.
- In-situ 3D structure fabrication to reduce the need for complex processes or a large number of separate steps.
- Reduce or subdue the use of templates to reduce the complexity of fabrication.
- Avoid additional high-temperature post-processing steps to reduce the energy required and cost of fabrication.

By comparing each of the different fabrication strategies against these five criteria, a quantitative comparison of each can therefore be developed. These criteria however do not necessarily consider the subsequent deposition of active materials, which may or may not be required depending on each strategy.

To meet the first criteria, the 3D structure must directly contribute to the electrochemical function of the 3D MBs and MSCs. This criterion is especially important to determine the potential performance of fabricated MBs or MSCs, as the specific energy, capacitance and power capacity takes into consideration the total amount of energy storage material and the available surface area for capacitive storage [12]. A best-case scenario would feature materials and structures that can function as both current collector and electrode material [65]. Different fabrication techniques can therefore be compared based on whether the 3D structures fabricated can directly contribute to the electrochemical performance of the battery.

The second criterion can be met with a fabrication method that can form features in a wide range of length scales. The wider the range of length scales formed, the greater the degree of area enlargement possible by the fabrication method. Different fabrication methods are limited by the scale at which features can be formed. A review of recent reported 3D structures formed out of micro-machined/etched silicon substrates, for example, was found to be generally limited to feature sizes down to a few microns, while certain template and template-free methods featured feature sizes down to tens of nanometres [13, 21, 58, 60, 62, 63]. While larger feature sizes do not necessarily equate to lower AEFs, nanostructured features have been demonstrated to provide an additional surface area increase of 13 to 80 fold compared to planar structures

[58, 62]. Altogether, a hierarchical approach, with a mix of features of various length scales would provide the largest increases in surface area, with the increase in the total surface area a multiplication of surface area increase from nanostructures and microstructures [62]. Therefore, meeting the second criteria is important for high AEF and high-performance 3D MBs and MSCs.

In-situ fabrication of 3D structures is the third criterion (i.e. all structures fabricated where materials are originally deposited). This criterion reflects the potential cost of any method or strategy. An in-situ fabrication process necessarily involves less cost compared to a method involving many ex-situ processes, simply by removing costs involved in the transport and handling of intermediate products. Therefore, a process that can be done (almost) entirely in-situ would be more cost-effective and more attractive, which is especially important for low-cost IoT devices and wearables.

A fabrication method that meets the fourth criterion will not require a template for 3D structures. Fabrication strategies that do require a template would increase cost and process complexity, by adding additional steps to deposit, pattern (if needed), and then remove the template [15]. In the case of 3D features formed from etched silicon substrates, masks and photoresists are used in place of templates to photolithographically define features to be etched, which involves a similar amount of process complexity. Template-free processes would therefore potentially incur less cost and are therefore more desirable.

Cost and process complexity is also a major consideration in the fifth criterion. The fifth criterion is met when no uniform high temperature ($>100\text{ }^{\circ}\text{C}$) treatment of the whole structure is required. Not only do high-temperature treatments add additional costs (stemming from the high energy usage from heating), high-temperature treatments can also introduce substrate stability issues, and challenges with ex-situ processing which increases the complexity of fabrication and makes such treatments unattractive [12]. However, a distinction has to be made with laser-based processes, which can involve localised heating, which does not present the same process disadvantages as ex-situ uniform heating in ovens. Fabrication strategies without high-temperature post-processes are therefore desirable to reduce costs.

While not a criterion for comparison, an additional consideration to note is whether the fabrication processes used to form 3D structures that can be modelled deterministically or stochastically. In processes that can be modelled deterministically, the output of the process is fully determined by the initial conditions and the parameter values chosen. A degree of randomness, however, is inherent in stochastic process models. Depending on the needs of a particular 3D structure design, either one is chosen. For example, if the objective of a particular

3D structure is to ensure a homogenous charge-discharge profile across the whole 3D MB, a deterministically modelled process, such as silicon micromachining or laser interference lithography (LIL) would be appropriate [5]. However, if the aim is simply to maximise the surface area of an electrode, a semi-deterministically or stochastically modelled approach, such as using self-assembled polystyrene templates, or growing nanostructured active materials might be simpler to implement [66]. The choice of using a deterministically or stochastically modelled process, therefore, depends on the particular objectives of fabrication.

With the rationale for each of these criteria developed, the next section will review in detail various examples of each strategy, and whether the various key criteria are met by each strategy. This review, along the following review of direct femtosecond-based processes, will be summarised at the end of the literature review to facilitate comparison between the various strategies.

2.3 Current strategies to fabricate 3D structures

2.3.1 3D MBs and MSCs from micro-machined or etched silicon substrates

Out of the four broad strategies, silicon micromachining is one of the oldest strategies used to fabricate 3D MBs and MSCs that can be modelled deterministically [67]. Silicon is attractive because high-temperature processes are not a major consideration for silicon substrates, which can withstand the extreme temperatures used in ALD ($< 400\text{ }^{\circ}\text{C}$) and CVD ($600 - 1000\text{ }^{\circ}\text{C}$) processes for subsequent deposition of MB & MSC thin films [58, 63, 68]. More recent research from showcases other feature types with feature sizes down to a single micron include trench designs, and arrays of single or double microtubes in silicon substrates formed from photolithography and reactive ion etching (RIE) [13, 14, 58, 63]. This significant improvement in feature resolution results in considerable increases in AEF, from 30 to 53 (**Figure 2.5**), and corresponding improvements in energy capacity and capacitance [58, 63]. A stochastic variant was demonstrated recently for 3D MBs which used the anisotropic etching properties of silicon to form Si microporous columns with AEF 14. These columnar structures were found to show a 250% increase in energy capacity ($375\text{ }\mu\text{A h cm}^{-2}$) over bulk Si ($150\text{ }\mu\text{A h cm}^{-2}$) [69].

Two key limitations, however, hinder the scalability and cost-effectiveness of this strategy. Micromachined substrates are generally limited by minimum feature sizes on the micron scale. In some cases, this limitation is an intentional design choice, as materials must be deposited with a minimum thickness to avoid short-circuits [70]. In other cases, however, cost and process complexity moving beyond 1 micron is a prohibitive factor [58, 69]. Due to these or other

reasons, few to no MBs or MSCs based on micro-machined/etched 3D silicon substrates alone have been demonstrated with features below 1 micron (not including grown nanostructures), limiting further increases in active surface area.

Silicon substrates are also usually limited to use as a mechanical support structure, instead of an active material. In MBs in particular, this limitation is caused in part by the large lithiation expansion (270%) of silicon when used as an anode material, which generally limits silicon anodes to nanostructures which can withstand lithiation related volume changes [35, 71]. Some strategies, like pre-lithiation of the silicon electrode, could allow the silicon microstructure itself be used as an anode without excessive volume cycling, but by and large micro-machined/etched silicon substrates are used exclusively as a mechanical support structure for MBs [72]. Furthermore, an additional diffusion barrier layer, such as TaN or TiN needs to be deposited to prevent lithium-ion diffusion into the silicon, if purely used as a mechanical support structure [73]. This diffusion layer, which must be thick enough to prevent lithium diffusion, adds to the amount of inactive material in MBs, and therefore would further reduce the specific energy and power of the overall battery. For MSCs, silicon is inactive alone, and is instead utilised in its micro and nano porous form, usually coated with a carbon-based or pseudocapacitive material coating for increased areal capacitance [74, 75].

While generally compatible with existing microelectronics fabrication processes, photolithography and etching processes, which requires the use of masks (templates) can be slow (few $\mu\text{m min}^{-1}$ for reactive ion etching [76]), expensive and requires many ex-situ fabrication steps. Fabrication might not be as costly if integrated into existing manufacturing lines. However, the complexity and overall cost of the photolithographic processes in general is still a major cost disadvantage.

To summarise, micro-machined/etched silicon substrates can be fabricated to form 3D structures that have high AEFs and feature sizes down to a few μm . Despite this hefty advantage, in most reported works the 3D silicon structure is used mostly for mechanical support, and the need for an additional diffusion layer adds to the amount of inactive materials in MBs and MSCs. Fabrication is also complex with multiple ex-situ processes, which reduces the cost-effectiveness of the overall strategy. Therefore, this fabrication strategy is a good starting point for 3D MBs and MSCs but is ultimately inadequate for cost-effective and scalable fabrication of high-performance MBs and MSCs.

2.3.2 3D MBs and MSCs from 3D templates

Nanostructures formed from various types of templates are currently the most popular method to fabricate 3D structures for 3D MBs and MSCs [3, 12]. These nanostructures can be used as

a current collector array for subsequent active material deposition or used to form nanostructured active materials directly. The three most popular template methods are nano porous anodic aluminium oxide (AAO) templates, self-assembling particle templates, and virus templates. The first method uses a self-assembled template made of nano porous anodic aluminium oxide (AAO) film, which can be modelled in a semi-deterministic manner [77]. Fabrication of the template is done at low temperatures (below room temperature) but can be done at higher temperatures (up to 50 °C) to increase the anodisation and formation rate of the template [78]. Pore diameters range from 10 to 400 nm, with pore densities of 10^8 to 10^{10} pores cm^{-2} [79]. In 3D MBs, the AAO template is usually deposited over a chosen substrate before a current collector such as nickel or aluminium is deposited on the template. The template is subsequently etched away, to reveal the nanostructured current collector array before electrode deposition (**Figure 2.6**) [80]. Various other materials including CuO on Cu, LiCO_2 on Al via sol-gel, and others have been demonstrated [81, 82]. 3D MSCs formed from AAO templates can be used to directly form nanostructured pseudocapacitive materials as well, bypassing the need to form a current collector array before subsequent deposition [83].

Figure 2.5. Fabricating 3D MBs from micro-machined silicon. (a) Schematic process for the fabrication of 2D and 3D MBs on silicon wafers through atomic layer deposition (ALD). (b) Various 3D constructions with increasing surface area, from micropillars (MPs) to single microtubes (SMTs) and double microtubes (DMTs). (c) Scanning electron microscope (SEM) images of DMTs and (d) SMTs etched from silicon wafers. Adapted from [58] with permission from Wiley-VCH.

The self-assembling of particle templates follows a similarly semi-deterministic approach [66]. As the colloidal solution containing nanometre sized polystyrene spheres are heated, the polystyrene particles self-assemble to form a reverse opal structure. A current collector deposited over the template, after which the template is removed via oxygen plasma etching or combustion. Researchers demonstrated an impressive 3D MB using this template method, which featured a nano porous 3D MB that had over 2,000 times the power density and twice the energy capacity of previously reported 3D MBs [15]. Alternatively, this template method can also be used directly with electrode materials with both MBs and MSCs [84, 85].

Virus templates are a stochastically modelled alternative, where genetically engineered viruses adsorb and self-arrange vertically onto metal surfaces to be used as a nano template. The viruses are then coated over with a current collector like nickel, to be deposited with active materials subsequently [60, 86]. Importantly, virus templates can also be used in conjunction with other fabrication strategies like silicon micromachining to improve AEF multiplicatively [62].

Figure 2.6. High-resolution transmission electron microscope (HRTEM) and scanning electron microscope (SEM) images of Al nanorods with deposited TiO₂. (a) HRTEM image showing the TiO₂ layer homogeneously covering the tips of the Al nanorods as well as (b) the gaps between nanorods. (c) HRTEM image showing the presence of a 4 nm thick layer of Al₂O₃ between the nanorod and the TiO₂ layer. (d) SEM images of the Al nanorods fabricated. Adapted from [80] with permission from the American Chemical Society.

The main limitation for templated 3D structures is in the additional process complexity inherent in the removal of template materials for AAO and polystyrene sphere templates, as well as the additional process steps required to form these templates in the first place. These multiple deposition, heating and drying steps also prevent the in-situ fabrication of these structures on existing devices. Template methods overall hold a lot of potential to form nanostructured large surface area electrodes, but the added complexity of multi-step fabrication still limits the cost-effectiveness of this strategy.

2.3.3 3D MBs and MSCs from template-free nanostructure growth

Instead of using templates to form current collector arrays, a direct approach can be used to grow active electrode materials directly onto current collector substrates, reducing the need for multiple deposition and removal steps. A wide variety of methods, such as hydrothermal growth or CVD have been demonstrated for template-free nanostructure growth, most of them sharing a need for high temperature ($< 100\text{ }^{\circ}\text{C}$) processing [17, 87-89]. For example, TiO_2 nanosheets were grown directly on carbon nanofiber sheets demonstrated via hydrolysis and condensation of the titanium precursor at $150\text{ }^{\circ}\text{C}$ for 3D MBs (**Figure 2.7**) [90].

Figure 2.7. Schematic of the formation of $\text{TiO}_2(\text{B})/\text{activated carbon fibre (ACF)}$ hybrid electrode. Fabrication begins with the formation of the ACF by electrospinning, followed by thermal activation in CO_2 . (Step I). Next, $\text{TiO}_2(\text{B})$ nanosheets are grown directly on the ACF through the hydrolysis and condensation process (Step II). Finally, the crystallinity of the $\text{TiO}_2(\text{B})$ nanosheets is improved by thermal annealing in air (Step III). Reproduced from [90] with permission from Wiley-VCH.

This similarity, however, is the major limitation for template-free nanostructure growth. Multiple ex-situ heating processes are often required, increasing the overall cost and complexity of the process. The high temperature and often harsh conditions for nanostructure growth also remove any possibility for in-situ fabrication. These nanostructure growth methods can be combined with other methods to form hierarchical structures, but a key consideration is that the structures formed from these other methods must be compatible with the harsh growth conditions for these nanostructured electrodes. Despite a clear potential for forming high AEF nanostructures of active materials directly, template-less nanostructure growth methods are limited in cost-effectiveness and scalability.

2.3.4 3D MBs and MSCs from the in-situ deposition of active materials

More recent research into 3D MBs and MSCs have leveraged on the rapid development of additive manufacturing technologies, especially in-situ deposition processes such as inkjet printing and extruder based deposition, or robotic dispensing (robocasting) [22]. These methods, along with related direct deposition methods such as laser induced forward transfer (LIFT) compose the fourth strategy under review. The key difference between these methods and other types of thick and thin film deposition strategies such as ALD, LbL or screen printing is the ability to fabricate arbitrarily designed 3D structures without the need for a mask or template.

Both thick and thin extrudates (analogous to thick and thin films) can be deposited, depending on the method.

A schematic detailing the deposition processes of all three methods are depicted in **Figure 2.8**. All three methods in this strategy share key similarities, in that they are all deterministically modelled, in-situ, single step ink (active materials) deposition processes that are automated. The main difference between the methods instead is the deposition (and transfer) mechanisms of each method. Inkjet printing is a process where low viscosity inks containing mixtures of electrode particles and conductive binders are deposited in picolitre droplets via heating or a piezoelectric actuator. Inks are deposited in-situ layer by layer in three dimensions either by the movement of the inkjet print head, or the sample stage. Various common 3D MBs and MSCs materials and even full MBs and MSCs have been printed [57, 91, 92]. Compared to robocasting, inkjet printing can be used to deposit thinner films, although not as thin as materials deposited by LIFT.

LIFT is similar to inkjet printing, in that individual ink droplets are deposited onto a substrate. However, laser pulses are instead used to transfer the ink, which is first deposited on a donor slide. Energy from the laser pulse is either absorbed by the ink or by an intermediate dynamic release layer, which then causes the ink to be ejected from the slide via heating or phase change forces onto a substrate [93]. LIFT has successfully used to transfer many different MB and MSC materials, including graphene, LMO, LCO and a solid-state electrolyte based on TiO_2 nanoparticles in an ionic liquid matrix [23, 25, 94-96]. However, further advances in material preparation would also have to be made to print thicker structures, to overcome material limitations from the low viscosity ink.

Instead of depositing individual droplets, semi-solid inks are prepared and extruded in a continuous stream via a narrow nozzle in successive layers to form 3D structures through robotic dispensing or robocasting. Robocasting is an extrusion-based technique, similar to fused deposition modelling (FDM) technology [22]. Inks can be extruded in a variety of ways, including using pneumatic, piston or screws systems. Compared to LIFT and inkjet printing, much larger and taller 3D structures can be formed because the more viscous ink is more mechanically stable, thicker, and able to hold the weight of following layers. The larger and taller 3D structures result in a larger available surface area for better material utilisation, but at the cost of resolution and film thickness due to relatively large nozzle diameters (down to 30 μm) [18]. Various 3D MBs and MSCs have been demonstrated, mostly designed with interdigitated electrode structures [18, 19, 56].

Together, these three techniques represent a fabrication strategy that can directly deposit active materials into arbitrarily designed 3D structures. However, two key limitations prevent full adoption. Firstly additional ex-situ post-deposition high temperature (up to 600 °C) heat treatments are generally required after deposition to improve mechanical stability and remove solvents/binders from deposited inks [18]. This additional step severely reduces the cost-effectiveness of this fabrication strategy. Secondly, printed materials require a significant amount of pre-processing or preparation to design ink formulations (active material plus binder/additive) for specific viscoelastic properties and the need for mechanically stable inks that can support multiple layers after deposition. For example, highly viscous and shear-thinning inks are needed for extrusion-based processes like robocasting, while low viscosity inks are required for drop-by-drop deposition from inkjet printing [97]. Other concerns include the retention or even enhancement of the electronic and ionic conductivity of deposited inks, which directly affects the electrochemical performance of printed devices [22]. Greater adoption of these methods will require more research and development into cost-effectiveness and ink.

Figure 2.8. Schematic of three in-situ deposition methods. From left to right: laser induced forward transfer (LIFT) using pulsed lasers, inkjet printing using either a heater or piezoelectric actuator and robotic dispensing (robocasting) using either air (pneumatic), a piston, or a screw. Reproduced from [22] with permission from Wiley-VCH.

2.3.5 Other methods to form 3D MBs and MSCs

Besides the four broad strategies reviewed above, other less common methods have been used to fabricate 3D structures with high surface areas such as aerogels ($600 \text{ m}^2 \text{ g}^{-1}$) or carbon foams [98]. These structures are then used as mechanical support structures and current collectors (in the case of carbon foams), before active materials are deposited via deposition strategies like LbL assembly or electrodeposition. Such structures are polymer-based, with the main limitation being the need for multiple chemical process steps to form these highly networked and porous materials.

While most methods are used to fabricate 3D structures from the electrode or current collector material, an alternative approach is to fabricate 3D electrolyte instead [84]. While this method might be potentially useful to fabricate 3D MBs and MSCs with minimal need for inactive materials, there is still a lot of room for improvement in the capacity and cycling capability of demonstrated cells.

To summarise this review of conventional fabrication strategies, none of these strategies present a good option for the cost-effective and scalable of fabrication of high-performance 3D MBs and MSCs. Alternative strategies are required to meet these needs, and as introduced at the start, femtosecond laser processes are an attractive alternative. To elaborate on that claim, the next section will begin with fundamental femtosecond laser concepts, followed by a review of the two femtosecond laser processes that will be under investigation in this thesis: femtosecond direct laser writing (fsDLW) and femtosecond laser interference lithography (fsLIL).

2.4 Femtosecond lasers and laser-material interaction

2.4.1 From continuous wave to femtosecond lasers

Since the first demonstration of monochromatic laser emission in 1960 by Maiman, lasers have transformed into an indispensable tool for a wide array of applications in communication, manufacturing, measurement, sensing, surgery and defence [99]. Lasers, in their simplest form, consist of an active lasing material placed in a resonator cavity. When the active material is pumped by an energy source, photons are generated which are then bounce within the resonator cavity, inducing more generated photons. These photons leave the resonator cavity via the output coupler, producing a beam of highly collimated, monochromatic and spatially and temporally coherent photons. Photon emissions in the lasing material are due to the stimulated emission of photons, from the downward energy transition of atoms in the active material. For sustained stimulated emission, the laser's active material is induced into a state of population inversion by optical, electrical or heat energy (from the energy source), such that the number of high energy atoms is greater than the number of low energy electrons. At sufficiently high output intensities, these emitted photons can remove material, induce phase changes and otherwise alter the material when focused or otherwise spatially and temporally manipulated on a material's surface.

Lasers can be classified in various ways, from differences in emission wavelength (λ) in the UV, VIS, IR spectra, to differences in emitted intensity (high versus low-intensity lasers). A useful categorisation, however when using lasers to manipulate materials is by categorising lasers by the length of the pulses emitted from the laser, from the emission of pulses in a

continuous wave (CW) to pulses that are microseconds to femtoseconds (10^{-15}) and even attoseconds (10^{-18}) long [100]. Below pulse durations (τ_p) of one picosecond, lasers are categorised as ultrafast. Ultrafast lasers induce unique laser-material interactions, made possible by the massive compression of energy in each pulse. Femtosecond lasers in particular have been subject to extensive research and development, and is today established as a commercial standard for highly precise and athermal manipulation of materials [101]. Focused femtosecond pulses can have peak energy intensities in the order of giga and terawatts with pulse energies of only micro or nanojoules. When a femtosecond pulse impinges on the surface of a material, this large amount of energy (enough to directly ionise materials) is transferred into the material quicker than heating can take place. This energy transfer results in non-linear phenomena such as athermal ablation, self-focusing in transparent materials, or multiphoton absorption in dielectric materials, which can then be harnessed for the fabrication of 3D MB and MSC structures.

To understand how femtosecond lasers can be used to fabricate such structures, the fundamentals of a femtosecond pulse and its formation must first be discussed. The femtosecond pulse can be described as a wavefunction with a central frequency ν_0 in **Equation (2.3)** [102]:

$$E(t) = A(t) \cos(\Phi_0 + \omega_0 t) \quad (2.3)$$

where $E(t)$ is the electric field strength varying in time, $A(t)$ is the envelope function containing the electric strength variation, and $\omega_0 = 2\pi\nu_0$ is the central angular frequency with phase Φ_0 . Assuming a simple envelope function, τ_p can therefore be captured by the full width at half maximum (FWHM) of the envelope of the temporal intensity function $I(t)$ (under the plane wave assumption) in **Equation (2.4)** [102]:

$$I(t) = \frac{1}{2} \varepsilon_0 c n A(t)^2 \quad (2.4)$$

where ε_0 is the vacuum permittivity (8.85×10^{-12} F m⁻¹), c the speed of light (3×10^8 m s⁻¹), n the refractive index, and an averaging factor 1/2 across all oscillations (**Figure 2.9**). The amplitude of the envelope function $A(t)$ can therefore be described (for $n = 1$) as in **Equation (2.5)** [102]:

$$A(t) = \sqrt{\frac{2}{\varepsilon_0 c}} \sqrt{I(t)} \approx 27.4 \sqrt{I(t)} \quad (2.5)$$

As femtosecond pulses are more commonly emitted in a Gaussian distribution, further adjustments to these equations have to be made, but for a first approximation the single dimension plane wave approximation is valid, especially since the width of the beam waist ω_0

incident on a material is usually much larger (in microns) than the actual interaction depth (in nanometres) in highly absorbing materials [103].

Figure 2.9. Femtosecond pulse shapes. (a) Electric field strength variation ($E(t)$) in an envelope ($A(t)$) of a femtosecond pulse, with τ_p at the FWHM of 5 fs. (b) Up-chirped femtosecond pulse. (c) Down-chirped femtosecond pulse. Adapted from [102] with permission from Springer Nature.

Unlike nanosecond or microsecond pulses, which can be easily formed via Q-switching (manipulating the gain in the laser cavity with active or passive control elements), the generation of picosecond and femtosecond pulses requires a more sophisticated mode-locking technique. Using Fourier transformations, any waveform can be shown as a combination of many related modes. The duration of a pulse is inversely proportional to the width of the spectrum (involving the modes), therefore a large number of modes are needed to form ultrashort pulses. In practice, these modes are formed through mode-locking, where an active medium (such as titanium sapphire (Ti:S) lasers with a central $\lambda = 800$ nm, or a Yb fibre with fundamental $\lambda = 1030$ nm) with a large gain bandwidth is placed in a cavity with an active (optical modulator) or passive (saturable absorber) element. A large number of synchronised longitudinal modes can then be formed and made to interfere to form a train of highly compressed ultrashort pulses [104].

Mode-locking, however, only generates pulses with low to moderate amounts of energy [104]. To further increase the amount of energy and shorten the pulses available, a method of pulse amplification called chirped pulse amplification (CPA) is used [105]. When femtosecond pulses propagate through various media such as glass or even air, different spectral components (corresponding to different modes) that make up the mode-locked femtosecond pulse are dispersed. This dispersion results in a temporal broadening of the pulse from the linear increase (up-chirped) or decrease (down-chirped) of the frequency of $E(t)$ over time. Chirp can be described by an additional time-dependent phase function ($\Phi_a(t)$) to the temporal phase term (**Equation (2.3)**) such that **Equation (2.6)** is followed [102]:

$$\Phi(t) = \Phi_0 + \omega_0 t + \Phi_a(t) \quad (2.6)$$

and by defining the momentary or instantaneous light frequency $\omega(t)$ such that **Equation (2.7)** can be described as [102]:

$$\omega(t) = \frac{d\Phi(t)}{dt} = \omega_0 + \frac{d\Phi_a(t)}{dt} \quad (2.7)$$

Temporal broadening from chirped pulses is generally viewed as detrimental to pulse control especially at pulse lengths in the tens of femtoseconds. In CPA however, pulses are temporal broadened (up to a factor of 10^3 to 10^5) by introducing chirp to the pulse using a series of diffraction gratings. Nonlinear phenomena which would have otherwise led to the degradation of beam quality and even damage to laser components is avoided, and laser intensity can be safely magnified by several orders of magnitude. An opposite chirp is then reintroduced to the amplified pulse to compress the pulse to its original length, before being emitted from the laser cavity. Therefore, with the introduction of mode-locking and subsequently CPA, high-powered and ultrashort femtosecond pulses can be produced, opening up new possibilities for laser-material interaction [104].

2.4.2 Femtosecond laser-material interaction

Understanding the effects and mechanisms of controlling femtosecond laser-material interactions will be important for utilising femtosecond lasers to form 3D MB and MSC structures. These parameters are analysed in detail in this section.

Wavelength

Across the electromagnetic spectrum, the wavelength (λ) of a particular electromagnetic wave is simply the function of its energy according to the photon energy equation in **Equation (2.8)**:

$$E = \frac{hc}{\lambda} \quad (2.8)$$

where h is Planck's constant ($6.63 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$) and c is the speed of light. In the visible light spectrum, λ is usually measured in units of nanometres (nm). λ is generally determined by the active medium used, but through harmonic generation, wavelengths shorter than the fundamental wavelength can be generated. When N ($N \geq 2$) photons from a single wavelength interact with a nonlinear crystal, the photons are combined to form a new photon with $1/N$ the wavelength, and N times the energy. The new beam is then termed the N^{th} harmonic. However, because of losses in these crystals, these harmonics often have poorer beam characteristics and lower intensity pulses.

Wavelength control is important to fabricate useful 3D MB and MSC structures. When photons from a laser impinge on a material, photons can be either absorbed, transmitted or reflected through the material, depending on the absorptivity spectrum of the material. Material structuring can only occur when energy from the photons are absorbed by the material.

The type of interactions depends on the energy and intensity of the photons, as well as the optical properties of the material. At intensities below 10^9 W cm^{-2} , or below the threshold for nonlinear phenomena, electrons in dielectric materials can only directly absorb photons in the conduction band [106]). Electrons in the valence band, therefore, must be electronically excited by photons of energy E corresponding to the optical bandgap between the conduction and valence bands before absorption can occur to change the material. This bandgap disallows intermediate electronic transitions, rendering materials such as glass or silica transparent to most λ in the visible (400 – 800 nm) visible range. Only when electrons are excited into the conduction band can they absorb energy via collisions with nuclei (inverse bremsstrahlung) and cause further electronic transitions from the valence band [107]. Polymers behave similarly with the optical bandgap analogous to the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of a polymer. Metals, in contrast, have free electrons in the conduction band, therefore absorption of photons of most λ in the visible, ultraviolet (UV) and infrared (IR) spectrum can take place [107]. The high reflectivity of most metals, however, reduces photon absorption significantly, which affects the actual absorptivity spectrum of any metal.

Ultrashort pulses can be used to surpass these limitations, to a certain degree. Ultrashort pulses emitted from femtosecond lasers can have intensities in excess of $10^{13} \text{ W cm}^{-2}$, such that the probability of the simultaneous absorption of two or more photons (two- or multiphoton absorption) is significant. Electronic transitions in dielectrics across optical bandgaps in the interaction region (into the conduction band) are therefore possible for more wavelengths provided the photon energy is an integer multiple of the bandgap energy. At even higher intensities, generation of free electrons can occur via avalanche ionisation, where distortion lowers the potential barrier for electron escape. Ionisation via electron tunnelling can then dominate over multiphoton ionisation. Subsequently, excited electrons in the conduction band can absorb energy via inverse bremsstrahlung and escape, and collide with valence band electrons to cause an avalanche of electrons excited into the conduction band [108]. Furthermore, in a tightly focused beam, both ionisation mechanisms are initially limited to regions smaller than the diffraction limit, where the probability density of simultaneous or tunnelling absorption is the greatest. This feature of nonlinear absorption is taken advantage of in the two-photon polymerisation (TPP) process (under the umbrella of DLW), where previously unachievable nanometre sized features are formed by polymerisation using a tightly focused ultrashort pulse laser [109]. Nonlinear absorption via ultrashort pulses therefore not only allows a wider range of wavelength options for optically transparent dielectric and polymeric material but can offer finer feature sizes. The wavelength, however, still plays a

significant role in how efficient these processes are. Therefore, choosing an appropriate laser wavelength of a laser important for cutting, treating or otherwise modifying different materials.

Pulse duration

While λ is a parameter common to all types of lasers, pulse duration (τ_p) is only important when considering pulsed lasers. As introduced in the previous section, the length of a (simple) pulse is determined to be the FWHM of the pulse envelope $A(t)$. In laser-material interaction, the length of the pulse determines the interaction time of the material; in effect, τ_p is the amount of time it takes for the pulse to be fully absorbed by the material. When electromagnetic waves interact with a material, a cascading series of processes occur, each taking a certain amount of time. An overview of these processes is covered in **Figure 2.10**. Starting with initial absorption of photons at 10 to 100 femtoseconds, energy from the excited electron is then transferred into the lattice or molecular structure of the material through phonon scattering after 1 picosecond before thermal energy is dissipated through the rest of the material via diffusion above 100 picoseconds. With enough energy, thermal diffusion can also lead to phase changes or the initiation of photochemical processes throughout the material.

Ultrashort pulses interact with materials in the order of picoseconds to femtoseconds, short enough that all the energy in a pulse can be absorbed by electrons before the transfer of energy to the rest of the lattice can occur (**Figure 2.10**). The lattice, therefore, stays “cold”. This process would result in an absorbed energy density W_{abs} at the end of the pulse only to the electrons, such that it follows **Equation (2.9)** [110]:

$$W_{abs} = \frac{2A \cdot F}{l_{abs}} \quad (2.9)$$

where A is the absorption coefficient, F is the fluence of the pulse (discussed in detail in a later section) and l_{abs} is the absorption depth of the laser into the material, often in the order of tens of nanometres [110]. At F above ablation thresholds, ionisation of the material can also occur simultaneously in the same femtosecond timescale [111]. Assuming all losses are negligible and no changes to the optical and electronic properties of the material, in the timescale of picoseconds all the absorbed energy of the pulse is then transferred to the lattice of the material. Shockwave propagation through the material from confined stresses come next, followed by thermal diffusion and finally phase change in the material, as energy from the pulse slowly dissipates throughout the rest of the material at the nanosecond timescale. By quickly transferring energy to electrons while the rest of the material remains cold, nonlinear phenomena such as athermal ablation are possible, where the material is removed without heating the lattice. The addition of phenomena such as athermal ablation effectively broadens the range of tools available for researchers to fabricate 3D MB and MSC structures.

Figure 2.10. Photon-material interaction timescales from femtoseconds (10^{-15}) to microseconds (10^{-6}). Adapted from [112] with permission from Springer Nature.

Fluence

Without enough photons, nonlinear phenomena cannot occur. When considering a pulse as a simple disk, fluence (F) is the measure of pulse energy (E_p) delivered across the diameter of a Gaussian beam (ω) at $1/e^2$, measured in units of J cm^{-2} as in **Equation (2.10)**:

$$F = \frac{4E_p}{\pi\omega^2} \quad (2.10)$$

Pulse energy (E_p) can be calculated from the average power of a femtosecond beam (P_{avg}) by dividing by repetition rate (f) in **Equation (2.11)**:

$$E_p = \frac{P_{avg}}{f} \quad (2.11)$$

The peak intensity (I_{peak}) of a pulse, which, as discussed above is commonly used to determine the threshold for nonlinear phenomena can then be calculated from peak pulse power (P_{peak}). Peak pulse power is itself is calculated from the pulse energy divided by τ_p in **Equation (2.12)**:

$$I_{peak} = \frac{4P_{peak}}{\pi\omega^2} = \frac{4\left(\frac{E_p}{\tau_p}\right)}{\pi\omega^2} \quad (2.12)$$

Therefore, F is simply the peak intensity multiplied by τ_p .

Fluence can be used to control various laser-material interactions. For example, with enough F , compressive stresses are generated by the pulses impinging on the material and confined within the local interaction area [113]. This stress confinement occurs when τ_p is less than the time it takes for energy to be transferred to the rest of the material. Accumulation of these stresses can lead to the generation of a tensile wave that can form subsurface voids, which leads to the

separation and ejection of a layer of material. This layer-wise removal is commonly known as photomechanical spallation, evidence of which can be observed by the layered appearance of ablated surfaces [107]. With further increase above the spallation threshold, athermal, or cold ablation can occur, as opposed to ablation by explosive boiling by longer pulse lasers [114]. The absorption of a large amount of energy results in a build-up of electrostatic (Coulombic) forces that cause the expulsion of material without “heating” up the lattice. However, once enough time has passed and more energy is transferred to the lattice, ablation from phase explosion can occur. Overheating of the surface region from increased fluence leads to rapid decomposition of the melted material into an explosive mixture of vapour and liquid droplets, with both of these processes (among others) contributing consecutively to material removal [107, 111]. With athermal processes like cold ablation, clean, precise and localised material removal is possible, with minimal damage from reduced heat diffusion into the surrounding area. Fabrication and structuring of 3D MB materials can therefore be done with more precision. For example, a femtosecond laser was used to ablate a $\text{Li}(\text{NiMnCo})\text{O}_2$ electrode, forming high aspect ratio 3D structures without melting or otherwise damaging the underlying electrode material [115]. Control over femtosecond fluence, therefore, enables the use of a wide range of different processes that can be used fabricate 3D structures.

No. of pulses

When a single ultrashort pulse is absorbed by different materials, there are various fluence thresholds where reversible and irreversible changes can occur to the material. Metals, for example, have a threshold for melting and ablation at various regimes, while transparent dielectrics have various damage thresholds, including plasma, permanent and visible damage [111, 116]. These thresholds, however, can be significantly lowered with an increasing number of pulses (N) incident on the material, caused by an accumulation of laser induced defects. The observed lowering of thresholds is known as the incubation effect, and the incubation-dependent threshold (F_{th}^N) for metals and polymers can be estimated from **Equation (2.13)** [117, 118]:

$$F_{th}^N = F_{th}^1 N^{\xi-1} \quad (2.13)$$

where ξ is the experimentally determined incubation factor, and F_{th}^1 is the threshold fluence from one pulse. Thermal stress-strain energy storage was found to be the incubation mechanism in metals, while the incubation mechanism in polymers is highly dependent on the complex interaction of material properties and light. The incubation effect for dielectrics however was found to level off after a large amount of pulses, and can be estimated from **Equation (2.14)** [117, 119]:

$$F_{th}^N = F_{th}^\infty + (F_{th}^1 - F_{th}^\infty) \exp[-k(N - 1)] \quad (2.14)$$

where F_{th}^∞ is the fluence threshold after an infinite number of pulses, and k is the incubation factor. Practically, a large number of pulses is often used for device fabrication over a large area, to reduce the amount of energy needed per pulse. Understanding the mechanisms and methods to estimate the actual threshold is therefore important for reproducibly scalable manufacturing.

Repetition rate

The rate at which pulses are emitted from an ultrashort laser is known as the repetition rate (f), in Hz. f is usually fixed by the design of the laser, but can often be reduced and therefore controlled externally [104]. Control can be achieved by employing a synchronised (mechanical) chopper or electronic signals sent to the laser controller. High f (generally 1 MHz and above [120]) can theoretically enable high rate machining, exposing a certain N per unit area to the material. Mechanical instabilities within optical scanning systems, however, limit the maximum speed of scanning [111].

The effect of f varies tremendously based on the material and the specific laser-material interactions. Even within the same type of material, differences in melt dynamics, or material properties could lead to entirely different results. An increase in f for Ti machining was discovered for example to increase the accumulated pulse fluence threshold for surface microstructure formation. Conversely, the same increase in f for Cu machining resulted in a decrease in the accumulated pulse fluence threshold [121]. This difference was attributed to the speed of solidification between pulses, with Cu resolidifying between pulses while Ti stays in the liquid state. Pulses which could have contributed to defect accumulation in Cu were instead absorbed by the melt to form a dielectric-like state, which was posited to cause the reported increase in fluence threshold.

However, an increase in f (into the high f regime) generally results in a larger amount of thermal accumulation in the material, as a result of the long thermalisation (time for thermal diffusion to the rest of the material) in the microsecond timescale, especially in dielectrics (**Figure 2.11**) [112, 122, 123]. In poorly conducting materials such as dielectrics and polymers, accumulation can quickly lead to (often) deleterious heating and carbonisation [124]. Carbonisation in some polymers is useful, such as the fabrication of highly conductive ($15 \Omega \text{ sq}^{-1}$) porous 3D arrangement of graphene flakes by pulsed laser carbonisation for 3D MSCs, providing a simple method to form useful carbon-based 3D MBs and MSCs [125, 126]. Similar carbon-based MSCs have also been demonstrated using high f (1 MHz) femtosecond lasers

[28]. Examples like these highlight the importance of f in providing enough thermal accumulation for carbonisation to occur in ultrashort pulsed laser.

For other physical effects which can diffuse through a material such as pressure, increasing f is less likely to lead to pressure accumulation. Pressure accumulation from consecutive pulses can only occur if the period of two pulses is less than the stress relaxation time of a material, which is more likely to be in the order of hundreds of nanoseconds or even picoseconds in different materials [123, 127]. Only at very high f (in the MHz range) might pressure be accumulated in a similar manner to heat. However, the short τ_p of each individual pulse still means that each femtosecond pulse can induce highly localised stress in the laser interaction region. Investigations into the effect of f on different materials are therefore important for the control over laser-material interactions for 3D structure fabrication.

Figure 2.11. Effect of (a) low versus (b) high f on the accumulation of thermal energy and pressure. Reproduced from [123] with permission from Elsevier.

Polarisation

The effect of polarisation on laser micromachining has long been established, where variations in the reflectivity of s- and p-polarisation relative to the plane of incidence affect the absorptivity of light in materials [128]. Polarisation-dependent feature anisotropy follows, with linearly polarised light with elongated holes perpendicular to the direction of polarisation. Circularly polarised beams, in contrast, are isotropic in all directions, therefore are often used to improve machining quality in all directions [128]. The polarisation of a beam can be controlled by changing the design of the laser cavity, or externally via a combination of half-wave plates, quarter-wave plates, polarisers or Q-plates.

The same polarisation dependency follows with femtosecond laser micromachining, but the addition of nonlinear effects in femtosecond micromachining introduces new aspects of laser material interaction to investigate [129, 130]. For example, circular polarisation improved the

refractive index change in dielectrics when exposed to high (42 TW cm^{-2}) fluences above the tunnelling ionisation regime. Waveguide writing at lower intensities conversely resulted in larger refractive index changes when linearly polarised, reflecting the polarisation dependence on free carrier generation in different ionisation regimes [131]. Similarly, waveguides machined at high f were found to be polarisation independent [132]. A possible explanation could be that waveguide formation at higher f are based on thermal accumulation, instead of plasma formation induced by individual pulses [122]. The nonlinear formation of nanometre sized laser-induced periodic surface structures (LIPSS) from femtosecond laser irradiation is also polarisation dependent, forming ripples that are aligned perpendicular to the linear polarisation direction [133]. Circular polarisation, in contrast, was found to produce disordered nanostructures that varied in size [130]. Polarisation also plays a large role in the contrast of interference patterns formed through laser interference, which will be discussed in greater detail in a later section. By controlling the features of these nanostructures, changes in surface functionality can be achieved [134].

More recently, a new frontier of research in vector beams is open, enabled by advances in polarisation control. Whereas scalar beams exhibit the same polarisation across the cross-section of a beam (such as in circular or linear polarisation), vector beams exhibit spatially variant polarisations across the beam cross-section (**Figure 2.12**). The two most attractive vector beam polarisations under research today are radial and azimuthal polarisations. Micromachining with radial polarisation, in particular, has been found to improve cutting efficiency and cutting speeds by approximately 35%, made possible by the increase in absorption from the p-polarised beams in every direction relative to the cut surface [135, 136]. Similarly, radially and azimuthally arranged LIPSS structures have been demonstrated, enabling new application possibilities [137].

In summary, while there are no direct examples in polarisation control for 3D MB and MSC structures, polarisation control simply provides another tool to leverage on in future works.

Figure 2.12. Structures formed in fused silica from radially and azimuthally polarised femtosecond pulses. (a) & (b) Structures formed in fused silica after irradiation with multiple 300 nJ pulses and (c) & (d) multiple 500 nJ pulses. (e) Optical signature of structures formed in (f), observed under cross-polarised light. The scale bars are share between each pair of images. Reproduced from [138] with permission from the American Physical Society.

Besides these parameters, a more complete picture of femtosecond laser material interaction can be obtained by considering other parameters. These parameters include noise properties of the laser in terms of pulse, intensity and phase, beam quality and ellipticity, pulse quality and the time-bandwidth product. More details on these parameters can be found in a review by Paschotta [139].

Control over the wavelength (λ), pulse length (τ_p), fluence (F), number of pulses (N) and repetition rate (f) of femtosecond lasers can be harnessed for useful phenomena to fabricate 3D structures. However, to effectively fabricate useful 3D structures across a large area, these femtosecond pulses must be manipulated spatially and temporally. Femtosecond direct laser writing (fsDLW) and femtosecond laser interference (fsLIL) are two such useful methods for fabrication 3D MB and MSC structures.

2.5 Femtosecond direct laser writing (fsDLW)

2.5.1 Fundamentals and process parameters for fsDLW

fsDLW is a method that utilises a scanned femtosecond beam in two or three dimensions to alter, add or remove materials. Material manipulation can occur via different mechanisms, depending on laser parameters, and can be used to fabricate a wide variety of 3D MB and MSC structures. Furthermore, by combining material manipulation with material deposition hybrid manufacturing is achieved.

“Writing” is done by translating a focused laser beam across a flat plane, either with a galvano-scanner and f-theta lens or with a microscope objective coupled with an x-y motorised stage, depending on the feature size and fabrication speed required. The galvano-scanner set-up generally allows scanning across a larger at higher speeds, but with limited focusing due to the lower numerical aperture (NA) of the f-theta lens. A collimated beam is directed into the galvano-scanner, where two mirrors rotate to scan a beam across the Cartesian plane. Between the mirrors and the sample plane, a f-theta lens is used to focus the beam into a tight spot. A schematic of these two types of fsDLW set-ups is described in **Figure 2.13**. Laser parameters like F , λ , τ_p and f can be either controlled internally by the laser controller and software, or external components like attenuators, nonlinear crystals (harmonic generation) or beam choppers. Other parameters like polarisation can only be externally modified with components like polarisers and waveplates.

Figure 2.13. General schematic for fsDLW. (a) fsDLW via an objective lens and motorised sample stage. The laser beam is directed towards the objective lens and focused onto the motorised stage to write arbitrary patterns onto different materials. (b) fsDLW via a galvano-scanner and a x-y-z adjustable sample stage. The laser beam is directed into the galvano-scanner, where a set of rapidly rotating mirrors move the beam in the x and y directions, and a f-theta lens focuses the scanned beam onto a focal plane at the sample stage.

During the writing process, the effects of additional process parameters have to be accounted for. For example, the scanning speed of the beam (v) is directly related to the beam width at focus, F and N (for a given f) a particular part of the material is exposed to since a scanned line can be treated as a series of spatially overlapping pulses. A whole range of other process parameters, such as multiple exposures of the same area to a laser beam (multiple lasing), or ambient atmosphere (or lack thereof) can also decrease (increase) threshold of ablation, or change the decomposition/alteration products from laser manipulation [111, 140-142]. By leveraging on the different types of laser material mechanisms and interaction with varying laser parameters, fsDLW can be used in a variety of ways to fabricate 3D MB and MSC structures, to be reviewed in the next section.

2.5.2 fsDLW for fabricating and integrating 3D MB and MSC structures

fsDLW can be used to form in-situ 3D features at a wide range of feature sizes, and different mechanisms can be utilised depending on the laser and process parameters chosen. For example, fsDLW was recently used to “calendar”, or structure via athermal ablation the surface of deposited lithium cobalt oxide or LCO cathodes, and lithium manganese oxide, or LMO cathodes, forming microgrids in the material [23, 25, 95]. By selectively removing material to form 3D plateaus in the electrode material, calendaring was found to greatly improve the performance of the cathode materials compared to the as-deposited material. This effect was attributed to an increase in electrical contact and a decrease in ion diffusion path lengths. Critically, the lack of thermal damage from the 3D structuring process helped to preserve the electrochemical performance of the material. While a powerful tool, athermal ablation via fsDLW still requires the deposition of material before calendaring can be done.

The formation of PG structures from graphene oxide (GO) is also worth mentioning, even if it does require an additional deposition step. GO, a graphene precursor consisting of graphene sheets with oxygen groups in solution can be photoreduced (i.e. oxygen groups removed with photons) by femtosecond photoreduction [143]. By scanning a beam across a large area of GO, 3D defect-ridden reduced GO (rGO) with feature sizes in the nanometre and micrometre scale can be used for 3D MBs and MSCs [144]. These rGO devices can achieve up to 3.67 mF cm^{-2} for MSCs and $14.6 \text{ mA h cm}^{-2}$ for MBs [145, 146]. The additional deposition step required for GO patterning however, generally reduces the attractiveness of GO reduction as a target for research.

The formation of 3D graphene nanostructures from polymeric materials through fsDLW is an attractive alternative for 3D power sources. Formation of these graphene nanostructures or porous graphene (PG) structures does not require additional deposition of materials; instead,

these PG structures can be rapidly formed through fsDLW alone. Graphene, a 2D monolayer material (960 mA h g^{-1}), is a high energy capacity and high-performance alternative to standard graphite (372 mA h g^{-1}) anode materials for MBs [26, 35, 147]. Graphene is also an attractive high capacitance MSC electrode material due to the high permittivity values and large active surface areas [125, 148]. Reported PG MSCs demonstrate capacitance values ranging from 0.27 mF cm^{-2} to 4 mF cm^{-2} or greater with typical scan rates from 10 mV s^{-1} to 50 mV s^{-1} [7, 125, 149]. Therefore, for this research work, achieving capacitance of 0.3 mF cm^{-2} or more with fsDLW PG MSCs is an acceptable design goal to match performance of existing PG MSCs. Fewer PG MBs have been reported in comparison, however, but those that are reported have energy capacities from 0.15 to $0.28 \text{ mA h cm}^{-2}$ with and without any post treatment [150]. $0.15 \text{ mA h cm}^{-2}$ is therefore an achievable goal for this thesis, with a large room for improvement to match the performance of commercial graphite anodes ($2.5 - 3.5 \text{ mA h cm}^{-2}$) [151]. In summary, these material properties make PG especially attractive for the fabrication of 3D MB and MSC structures, as exemplified by the excellent performance of PG MBs and MSCs reported in literature.

The formation of PG is a stochastic process, forming multi-layer nanoporous graphene flakes up to tens of microns across arranged randomly in 3D from the rapid graphitisation of commonly available polymeric materials, such as polyimide (PI). PG formed from in this manner has been demonstrated multiple times as a high-performance 3D MSC material, with the potential to be a good 3D MB anode material as well [152]. Active 3D structures can therefore be fabricated in a single step without the need for additional heat treatments or materials processing. The morphology of PG could be further modified by control over process parameters, resulting in controllable 3D graphene arrangements for different requirements [149]. Integration of PG into flexible and stretchable devices is also possible, through elastomer transfer [7]. While the formation of PG has been demonstrated multiple times with DLW using long-pulsed CO_2 lasers, far less research has been done on PG formation from a lot less work done with fsDLW. Femtosecond lasers potentially bring advantages to PG that cannot be replicated with long-pulsed CO_2 lasers, such as additional thermal control with repetition rate or the formation of nanostructures via other nonlinear processes [153]. These advantages could potentially support greater integration of these PG 3D structures through in-situ fabrication for on-chip integration of 3D MBs and MSCs.

Besides these direct examples of 3D structure fabrication, fsDLW can also be used as an in-situ source of heat treatment, electrode cutting, and drying, reducing the need for external processes [154]. A summary of the features of fsDLW is tabulated in **Table 2.1**. Lastly, the fact that all these different processes described can be achieved in-situ with a sufficiently powerful and

flexible laser makes the fabrication of 3D PG structures from fsDLW as an attractive strategy for 3D MB and MSCs.

2.6 Femtosecond laser interference lithography (fsLIL)

2.6.1 Fundamentals and process parameters for fsLIL

Instead of a single train of pulses, fsLIL utilises the periodic superposition of two or more pulses to form 2D or 3D periodic intensity patterns, which can then be similarly used to alter different materials [155]. Mathematically, the time-independent intensity distribution of any arbitrary periodic patterns ($I_t(r)$) of a beam with intensity (I), amplitude (E), polarisation ($\hat{e}$), wavevector ($\mathbf{k}$) and phase (ϕ) can be defined as a set of Fourier terms in **Equation (2.15)** [156]:

$$I_t(r) = I_0 \left[1 + \sum_{j < i}^N V_{ij} \cos \left((\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r} + \phi_i - \phi_j \right) \right] \quad (2.15)$$

where I_0 is half of the summation of the intensities of each beam. I_0 is followed by the spatial-cosine term, which sums up the intensity distributions of each beam pair (i and j). The spatial-cosine term itself consists of a few terms; first, the contrast term (V_{ij}) between the two beams is described in **Equation (2.16)**:

$$V_{ij} = \frac{E_i E_j (\hat{e}_i \cdot \hat{e}_j)}{I_0} \quad (2.16)$$

where E_i and E_j are the respective amplitudes of each beam pair, and $\hat{e}_i \cdot \hat{e}_j$ is the polarisation product of the two beams. V_{ij} captures the visibility of the interference pattern, from a value of 0, where there is no difference between the peaks and troughs, and 1, at maximum visibility. Both intensity and polarisation play a role; the contrast is at a maximum when both beams have the same intensity and polarisation and zero when there is only one beam, or when linear polarisation is orthogonal. Maximum contrast is therefore desirable to achieve. However, to maximise contrast when considering more than two beams, methods to find optimal polarisation values have to be used, because the polarisation values for maximum contrast for one pair might reduce the contrast of another [157, 158]. Conversely, there is only one optimal value of I , when all values of I are the same. The second part of the spatial-cosine term is the difference in wave vector components ($(\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}$), which determines the direction and period of each 1D pattern formed per pair and the pattern period as a whole. Lastly, the phase difference ($\phi_i - \phi_j$), determines the position of the fringes along dimensional axis. Altogether, almost any periodic and even some aperiodic structures can be defined with full control over

these parameters [155]. The resulting pattern is therefore a summation of effects of the interference of different beam pairs, as can be seen from the example in **Figure 2.14**.

One other essential factor for interference, which is not captured in the previous equation is spatial and temporal coherence between pulses in interfering beams. Both temporal and spatial coherence are extremely important for interference; coherence between two beams can only be maintained for a certain amount of time τ_c , which can also be described in terms of coherence length (L_c). Therefore, should the path difference between two beams fall beyond a certain point described by L_c , interference cannot occur. L_c is described by **Equation (2.17)**:

$$L_c = c\tau_c = \frac{c}{\pi\Delta\nu} \quad (2.17)$$

where $\Delta\nu$ is the optical bandwidth, of the laser. Femtosecond pulses are generated from the interference of many overlapping modes, resulting in an optical bandwidth that is correspondingly large. Consequently, femtosecond lasers would have a correspondingly small L_c , on the order of hundreds of microns. While the fundamental equation governing pattern formation does not change with the length of the pulse used for interference, the practical effect is that it is much more difficult to interfere pulses from ultrashort pulsed lasers as opposed to a continuous wave or long pulse lasers. Once interference is achieved however, these high peak intensity pulses can then be used to directly pattern or otherwise manipulate materials to form 3D MB and MSC structures.

Figure 2.14. Interference patterns formed from three beams. (a) Three beams, two on the same plane and one in the orthogonal plane and their respective vector ($\mathbf{k}$) and polarisation ($\hat{\mathbf{e}}$) terms. (b), (c) & (d) Intensity variations formed from each beam pair. (e) & (f) Final result of the 2D intensity variations from the summation of intensities across each set. a represents the peak-to-peak distance. Reproduced from [155] with permission under the CC BY-NC-SA license from MDPI.

Experimentally, fsLIL can be achieved by splitting a beam into two or more beams, which are then directed towards a common interference plane for patterning to occur. While there are various types of set-ups for fsLIL, one of the most common is the umbrella set-up where each beam can be individually manipulated, allowing greater flexibility and reconfigurability of the system, coupled with finer control over each beam [155]. A wider range of designed 3D structures can therefore be formed.

2.6.2 fsLIL for fabricating 3D MB and MSC structures

Laser interference has been used to fabricate 3D MB and MSC structures to great effect, using the traditional photolithographic steps of coating, exposure, and development. For example, a 3D MB consisting of holographically defined electrodes patterned by the interference of four laser beams was demonstrated [30]. LIL enabled the authors to fabricate 3D structures easily and deterministically with the varying pore filling fractions and geometries, for easy and direct optimisation of electrochemical performance. Fully assembled, the 4 mm² MB could be cycled 200 times with only 12% capacity fade at 600 C, with an impressive energy density and power.

From this example, the deterministic design aspects of LIL are easily established. fsLIL in comparison has not been widely utilised, if at all for 3D MB or MSC structure fabrication at this moment. This lack of utilisation possibly due to the practical challenges in ensuring coherence for interference described previously. However, one key advantage of fsLIL over LIL that makes fsLIL a particularly attractive tool in 3D structure fabrication is the demonstrated possibility of directly patterning high aspect ratio patterns directly into optically transparent materials which is not possible with conventional LIL. Through non-linear laser-material interactions such as two photon absorption, high aspect ratio features could theoretically be formed in optically transparent materials such as glass or PDMS [159, 160]. These 3D patterns could then be logically used as 3D MB or MSC structures for further deposition of active materials [31, 161]. To fabricate useful patterns, a few constraints must be defined. First, a minimum pitch of 1 μm for these periodic structures can be determined from the reported minimal electrolyte thickness (180 nm). Below this thickness, electrolyte breakdown cannot be avoided even with perfect film deposition [70]. If 180 nm limit is similar for the other MB and MSC layers, a minimum pitch of 1 μm would therefore be needed to deposit all required layers. With this minimum pitch, achieving a theoretical AEF of 100 could be possible with a material thickness of 100 μm . Considering possible limitations in the actual fabrication process from this theoretical value (such as limitations in contrast between beams), a more practical target of 30 for AEF can be determined. Large AEF features could therefore be fabricated for 3D MBs and MSCs with fsLIL through deterministic design.

fsLIL shares many of the same advantages as fsDLW; both being femtosecond laser-based processes. With fsLIL, fabrication is in-situ and template free, with the ability to fabricate periodic structures at multiple scales down to near the diffraction limit. Depending on the material used, 3D structures made of active materials could also be formed. fsLIL could also be used to do almost everything another laser-based process like fsDLW could do, such as in-situ heat treatment. With an intelligent system design (such as controllable apertures, mirrors and lenses), fsLIL even be combined with fsDLW to leverage on the strengths of both methods. Therefore, while fsLIL is a currently untested process in 3D MB and MSC structure fabrication, its untapped potential makes fsLIL worth exploring.

In conclusion, fsLIL is a powerful strategy to design and fabricate 3D structures with well-defined and controllable features for 3D MBs and MSCs, especially through the potential patterning of optically transparent materials. A summary of the features of fsLIL is tabulated in **Table 2.1**.

2.7 Outcome of the Literature Review

Smart wearables and IoT devices cannot be effectively powered by current thin film 2D MBs and MSCs, due to limitations in energy capacity. A new approach is needed to fabricate effective power sources, by exploiting the third dimension to form 3D MBs and MSCs.

Through this literature review, fsDLW and fsLIL are established to be cost-effective and scalable alternatives for the fabrication of 3D MB and MSC structures, in contrast to current 3D MB and MSC fabrication processes, namely 3D structures formed from micromachined silicon substrates, from templates, from templateless growth, and from additive manufacturing. Comparison between these strategies is based on an established set of quantifiable criteria, where a cost-effective and scalable fabrication strategy must form active structures across a wide range of feature scales with in-situ fabrication, without the use of templates or ex-situ high temperature treatment. Both fsDLW and fsLIL can bring unique advantages to 3D structure fabrication, such as well-defined periodic structures with fsLIL, or rapid, active structure formation with fsDLW. Both also meet key criteria for scalable fabrication, being able to achieve in-situ, template-free fabrication of multiscale structures without the need for ex-situ high-temperature treatments. These features of fsDLW and fsLIL, in combination with additional advantages with process adaptability (the same laser can be used for fsDLW and cutting, etc) and easy integration with material deposition technologies (such as inkjet deposition) make fsDLW and fsLIL attractive candidates for further research and development into 3D MB and MSC fabrication. A summary of this comparison of conventional strategies and femtosecond laser strategies is presented at the end of this section.

A wide range of femtosecond laser parameters can be leveraged to control the manipulation of material and therefore the formation of 3D structures in materials. To fully utilise the breadth of flexibility a femtosecond laser affords, understanding of a few key parameters is essential. These key parameters, which are discussed in detail in this literature review, control different aspects of laser-material interaction, such as the control over the rate of heat accumulation within a material from irradiation (repetition rate) or the absorptivity of the material to laser pulses (wavelength). Therefore, by understanding and carefully controlling these parameters, the same type of femtosecond laser used for athermal ablation to form 3D relief in deposited cathode materials could also be used for the thermal reduction of GO or carbonisation and graphitisation of polymeric materials for 3D porous graphene MBs and MSCs.

Further research is required to understand how fsDLW and fsLIL could be utilised to develop high-performance 3D MB and MSC structures. As discussed in the literature review, fsDLW could be used to fabricate and integrate active 3D PG structures for both MBs and MSCs for on-chip integration on electronic devices. The performance of these structures is also highly dependent on high electrical conductivity and large surface areas. Therefore, one objective of this thesis is to research into and develop PG 3D MB and MSC structures that can be fabricated directly onto electronic devices. These 3D structures are targeted to have low sheet resistance ($50 \Omega \text{ sq}^{-1}$) for wide, easily accessible, and electrically conductive structures that can facilitate greater MB and MSC performance. These 3D structures should also be demonstrated in 3D MB and MSCs.

To achieve this objective, a fsDLW methodology to repeatably form uniform PG features first needs to be developed. Only with such a methodology would the influence of unwanted non-laser or process related parameters be reduced, such as the influence of acceleration and deceleration of moving components, or the influence of material changes during PG formation. This methodology will therefore facilitate consistent and repeatable formation of PG. The next step in achieving this objective is the research and development of a theoretical model that can enable the prediction of PG formation. Since PG formation is expected to be primarily driven by heating, the theoretical model should be able to predict the temperature rise in a precursor material such as PI based on the laser parameters used and the properties of the material. This theoretical model can then be accurately validated using the previously developed fsDLW methodology and characterised to determine optimised parameters for PG formation. Finally, in-situ fabrication of PG 3D power sources can be achieved by building and expanding on this theoretical model. By modelling the temperature rise at the top and bottom surfaces simultaneously, a thermally localised laser graphitisation (LLG) regime can be identified where heating is constrained only at the top surface of the PI while the bottom surface remains cool.

This LLG regime would therefore enable the in-situ fabrication of localised PG (LPG) on flexible and thermally sensitive substrates such as paper or polymers. 3D MBs or MSCs formed using PG or LPG should then be demonstrated, with performance matching or even exceeding other reported works on PG MBs or MSCs as discussed previously, with an expected energy capacity of at least $0.15 \text{ mA h cm}^{-2}$ or a capacitance of 0.3 mF cm^{-2} . With this research, the objective of fabricating high-performance 3D MB and MSCs structures with fsDLW can thus be achieved.

Parallel developments in fsLIL for 3D MB and MSC structures will focus on the direct patterning of optically transparent substrate materials. This approach will help to provide an alternative from fsDLW to developing 3D MBs and MSCs with periodic structures. As discussed in the literature review, fsLIL could be used to directly pattern complex periodic structures into the bulk of optically transparent materials. These structures can thus be formed in such materials for a greater surface area to deposit current collector and cathode or anode materials.

Achieving this objective will first require the research and development of a minimum two-beam fsLIL set-up that is designed for low angle ($< 10^\circ$) and large pitch ($> 1 \mu\text{m}$) patterning such that enough space is left for deposition of MB or MSC layers within the structure. This set-up must also use as few refractive components as possible to minimise energy loss through absorption and maximise patterning fluence. Lastly a simple calibration method needs to be developed for this set-up to ensure that pulses can interfere, given the low temporal coherence of femtosecond pulses. With this set-up and methodology, the modelling and fabrication of 3D structures in optically transparent materials is possible. These patterns with a pitch of $> 1 \mu\text{m}$ have to be formed through the bulk of a material at least $100 \mu\text{m}$ thick to achieve a theoretical AEF of up to 100 (assuming a pitch of $1 \mu\text{m}$). However, accounting for losses, a more practical AEF of 30 is targeted as a good design goal as discussed previously in the chapter. By achieving these targets, the overall objective of fabricating 3D MB and MSC structures can be achieved.

In the following chapter, the development of 3D MB and MSC structures will begin with the research and development of the fsDLW and fsLIL set-ups, methodologies, and instrumentation.

Table 2.1. Comparison of conventional and femtosecond fabrication strategies to fabricate 3D structures for 3D MBs and MSCs.

Strategy	Ref (MB & MSC)	Criteria					Features	
		Structure contributes to electrochemical performance	Feature scale	In-situ fabrication	Template is not required	No ex-situ high temperature (> 100 °C) treatment	Deterministic vs Stochastic model	Other remarks
Conventional strategies								
Micro-machined etched silicon substrates	[14, 58, 69]	N	mm – μm	N	N	N. A.	Deterministic	Fabricated via photolithography and etching
Templated 3D structures	[15, 62, 83]	Y	nm	N	N	Y	Both	Can be combined with other methods
Template-free nanostructure growth	[17, 90, 94]	Y	nm	N	Y	N	Stochastic	Can be combined with other methods
In-situ deposition of active materials	[20, 56, 91]	Y	μm	Y	Y	N	Deterministic	Material preparation critical
Femtosecond laser-based strategies								
Femtosecond direct laser writing (fsDLW)	[25, 28, 144]	Y/N	μm – nm	Y	Y	Y	Both	Alteration and removal of materials
Femtosecond laser interference lithography (fsLIL)	[30, 161]	Y/N	μm – nm	Y	Y	Y	Deterministic	Direct patterning can be done on various materials

Chapter 3: 3D material structuring with femtosecond lasers

In this chapter, the research and development of methodologies and system configurations to improve the reliability of patterning with femtosecond direct laser writing (fsDLW) and enable high fluence periodic patterning with femtosecond laser interference lithography (fsLIL) are detailed. The chapter begins with a discussion on a method to enable in-line monitoring of femtosecond pulses as pulses travel from the laser to each individual set-up. Next, a methodology to ensure the consistent and reliable formation of porous graphene (PG) structures with fsDLW is detailed. Lastly, the development of a fsLIL set-up to enable the in-situ patterning of $> 1 \mu\text{m}$ pitch patterns at high fluence with a simple calibration method is discussed.

3.1 Introduction

Femtosecond lasers are powerful tools to create 3D micro-battery (MB) and micro-supercapacitor (MSC) structures in a scalable and cost-effective manner. Creating 3D structures, however, requires additional manipulation of the beam such that any material manipulation can be finely controlled across a wide area and at a fine resolution through fsDLW, and fsLIL. Both fsDLW and fsLIL allow for the in-situ template-less fabrication of 3D MB and MSC structures, either through the formation of randomly arranged 3D nanostructures, or the patterning of defined periodic patterning. In this manner, femtosecond lasers can be used to create useful 3D MB and MSC structures for high-powered wearables and Internet-of-Things (IoT) devices.

Harnessing this power, however, is a challenge. Femtosecond pulses need to be manipulated spatially and temporally to create useful 3D MB and MSC structures, and fsDLW and fsLIL each face unique challenges in utilisation. Effectively utilising fsDLW requires the development of a process that can repeatably and consistently form and characterise 3D PG structures need to be overcome, to account for the uneven fluence during acceleration of the scanning mirrors [162]. The challenge facing direct patterning with fsLIL, on the other hand, stems from the low temporal coherence of femtosecond pulses [163]. Maintaining this temporal coherence for requires fine control over the path length difference between each beam path, which necessitates the development of a fsLIL set-up that allows for high fluence patterning while being flexible and simple to calibrate. Research into these processes and set-ups will encompass the digital designs, software, fabrication and characterisation, beginning with material preparation and selection of laser and process parameters.

3.2 Femtosecond laser – configuration, control & monitoring

The femtosecond laser itself is the most critical aspect in forming 3D MB and MSC structures. In this research work, the femtosecond laser used is Amplitude Systemes Satsuma HP ytterbium (Yb) fibre laser. The femtosecond laser is combined with a custom-built second and third harmonic generation system, enabling the generation of pulses at 1030 nm (fundamental), 515 nm (second harmonic) or 343 nm (third harmonic) at any one time. Femtosecond pulses from 220 fs to 10 ps can be generated. Maximum pulse energy is dependent on wavelength, owing to losses incurred by harmonic generation. Repetition rate can be varied from single shot to 2 MHz. Pulse output and other parameters can be controlled from the femtosecond software directly, but for this research work, laser parameters are controlled by in tandem with fsDLW and fsLIL process parameters. In this manner, fluence, number of pulses, repetition rate and wavelength can all be controlled by the laser.

3.2.1 Femtosecond pulse optical path and environment control

Maintaining control over the pulses and their environment is crucial for pulse stability, which is in turn critical for repeatability in forming 3D structures. The overall optical table set-up and a schematic of the beam path from the femtosecond laser are detailed in **Figure 3.1(a) & (b)**. Linearly polarised pulses with a Gaussian profile are emitted by the femtosecond laser are directed along an optical path via a series of mirrors. Different wavelengths leave at different locations on the output coupler, allowing independent manipulation of pulses in each wavelength, but with similar components across different wavelengths. Along the path, pulses are first directed through a half-wave plate, followed by a polarising beam-splitter and a subsequent half-wave plate. By controlling the angle of polarisation of the initial half-wave plate, the amount of energy transmitted and reflected within the beam splitter can be controlled (**Figure 3.1(b)**). This method allows in-situ manipulation of pulse energy, and reflected pulses are directed towards monitoring equipment for in-line monitoring of laser parameters (discussed in the next section). Un-reflected pulses continue through a second half-wave plate that can be rotated to change the subsequent linear polarisation of the pulses. Pulse lengthening due to dispersal of different spectral elements in femtosecond pulses and reductions in pulse energy from material absorption is minimised with the dominant use of reflective rather than refractive elements to elements such as mirrors to manipulate the beam path instead. Past the second half-wave plate, pulses are either be directed towards the fsDLW galvano-scanner set-up, or the fsLIL set-up by altering the beam path with a removable and adjustable indexing magnetic mount. To minimise any scattering or blockage of the pulses from the external

environment, the overall beam path and optical elements are protected by a dust-proof enclosure, dust filters and fume extractors. More details on the overall femtosecond laser system are available in **Appendix A**.

Figure 3.1. Femtosecond laser in-line monitoring. (a) Optical beam path from femtosecond laser output coupler (bottom right) to in-line monitoring set-up for 343 nm (dotted area) to fsDLW set-up (top left) or fsLIL set-up (top right). The whole system is custom built by the research team. (b) Schematic of the in-line monitoring system with the reflected beam from the polarising beam splitter (PBS). (R)M: (Removable) mirror. HWP: Half-wave plate. PBS: polarising beam splitter. GS: glass slide. PD: Photodetector. PM: Power meter. (c) Fluence and pulses captured by the PM and oscilloscope, respectively. Osc: Oscilloscope.

3.2.2 Femtosecond pulse in-line monitoring

Pulse quality and control can be further ensured by monitoring pulse properties within the beam path during the fabrication process itself. This control is achieved through a developed method and set-up to monitor three of the most important femtosecond laser parameters in-situ; repetition rate (f), pulse energy (E_p) and the number of pulses (N). Femtosecond laser parameters can be monitored within the optical path with (out of line) or without (in-line) disrupting the path itself. Of the two, in-line monitoring is preferred to provide a critical window into how laser parameters change during the fabrication process, or to verify that the correct laser parameters are being used without interrupting the fabrication process. Verifying that pulses are being emitted with the correct properties becomes even more difficult with parameters such as repetition rate and the number of emitted pulses, which travel and occur

within timescales shorter than the average human reaction time. In effect with in-line monitoring, deviations from the input parameters can be monitored and minimised to improve process reliability. Marking the occurrence of these deviations can also be used to account for variations in structure formation.

In-line monitoring of pulse parameters can be achieved by utilising the reflected beam from the polarising beam-splitter (**Figure 3.1(b)**). Repetition rate, number of pulses can be directly measured from is reflected beam through the beam-splitter. To monitor pulse repetition rate, a thin glass slide with minimal reflectivity (< 5%) is used to direct a small portion of the reflected beam into an appropriate photodetector (Thorlabs PDA36A-EC Si amplified detector). This low reflectivity beam splitter is used to prevent damage to the photodetector from high-intensity femtosecond pulses, especially during patterning at high fluence. Captured signals are then transmitted to an oscilloscope (Rigol MSO1104Z Digital Oscilloscope) for measurement and visualisation. Similarly, the number of pulses emitted by the laser can be captured and monitored through the same oscilloscope and photodetector by setting the oscilloscope up for intermittent rather than continuous capture.

Fluence, on the other hand, is much more difficult to directly measure from the reflected beam path. While measurements of repetition rate and the number of pulses are generally consistent across the reflected and un-reflected pulses, the amount of energy in each pulse between these two paths can differ widely depending on how much energy is directed through the polarising beam-splitter. However, in line measurement can be achieved with a single power meter, with sufficient calibration. The total amount of energy lost within the polarising beam-splitter and the glass side must first be measured at different incoming pulse energies to determine if the power loss is linear with pulse energy. The effect of pulse polarisation is not investigated because pulse energy is generally controlled through the laser control software (Eastern Logic MarkingMate) during experiments, for practicality. By determining the variation between input energy and monitored pulse energy, a calibration curve can be established where energy loss can be determined by calculating the difference between the total input energy (E_T) minus the sum of the reflected (E_R) and un-reflected (E_{UR}) pulse energies, such that $E_{loss} = E_T - (E_R + E_{UR})$. Therefore, by knowing the percentage energy loss and measuring the reflected average power of the reflected pulses, actual pulse energy can be determined calculated only from a single power meter and monitored through the fabrication process. An example of monitored pulses and average power (from which fluence can be calculated) is showed in **Figure 3.1(c)**.

Other parameters such as wavelength and polarisation, in comparison, are not likely to vary significantly during the timescale of fabrication, unless critical failure of the laser system occurs. Measurement of these parameters can therefore be done separately without the need for in-line

monitoring. In summary, protecting and monitoring femtosecond laser pulses provide the basis for cost-effective and scalable 3D material structuring.

3.3 3D material structuring on the femtosecond direct laser writing (fsDLW) hybrid manufacturing platform

Laser graphitisation is a highly versatile method to form graphene directly from carbon-containing polymeric (precursor) materials [125, 140, 142, 164]. Under laser irradiation, these precursor materials can be carbonised and graphitised in a single step to form laser induced graphene (LIG), also known as porous graphene (PG). PG is a randomised, 3D network of standing graphene flakes, while unconverted polymeric material supports the brittle graphene flakes below. These PG flakes are highly conductive and potentially biodegradable, with a large active 3D surface area distinct from single layer or multi-layer graphene [165, 166]. Compared to more established fabrication methods such as exfoliation, chemical vapour deposition (CVD), or chemical reduction, laser graphitisation lacks the precise nanoscale control over the formation of graphene with the trade-off between process flexibility and ease of fabrication [167]. Lack of nanoscale control, however, does not detract from the usefulness of PG; the plethora of reported PG sensors, energy storage devices, and even filters can attest to that [125, 126, 149, 164, 168].

Fabrication of arbitrarily designed MBs and MSCs with 3D PG micro and nanostructures can be achieved with fsDLW. After pulses exit the second half-wave plate after the polarising beam splitter, the pulses can be directed towards the fsDLW set-up when the mirror installed on the removable indexing mount is removed. The fsDLW set-up consists of a galvano-scanner, a f-theta lens mounted above a x-y sample stage. Pulses are directed upwards and towards the inlet of the galvano-scanner utilizing two 45° angled mirrors in a periscope arrangement. Within the galvano-scanner, pulses are directed in the x and y directions by means of two scanning mirrors working in tandem. Pulses are subsequently focused by a f-theta lens across a (curved) focal plane. An x-y sample stage is installed directly below the galvano-scanner to secure samples for writing. Arbitrary patterns of 3D micro and nanostructures can therefore be written into the samples, depending on the parameters chosen. Different galvano-scanners are used for the three wavelengths (1030 nm and 515 nm together, 343 nm separate) to reduce the downtime required for switching between mirrors and lenses across the two wavelengths. Scanning and other process parameters are generally controlled through commercial laser software control system. A galvano-scanner set-up is chosen instead of an objective lens-based set-up for more rapid writing over a larger area. The overall fsDLW set-up and writing process are shown in **Figure 3.2**.

Figure 3.2. Femtosecond direct laser writing (fsDLW) set-up. (a) Two galvano-scanners for all three wavelengths (343 nm, 515 nm & 1030 nm separate) mounted above x-y-z- adjustable sample stages. The second galvano-scanner (515 nm & 1030 nm) is hidden from view. The purple arrow marks the optical path the pulses travel into the galvano-scanner, and the white dotted area marks the 10 x 10 mm fsDLW area for 343 nm pulses. (b) Close-up of the 343 nm fsDLW writing area during the fsDLW writing process to form porous graphene (PG) sensors from polyimide (PI) tape.

3.3.1 fsDLW writing process for porous graphene (PG) structures

Several challenges need to be met to form consistent and repeatable 3D structures using fsDLW. Some, like the determination of the height of the focal plane from the f-theta lens surface, are based on the specific arrangement of the fsDLW set-up. Others are inherent to the fsDLW process itself, such as wrinkling and curling of patterned films from uneven heating and uneven fluence across scanned patterns due to acceleration and deceleration of scanning motors. An overall methodology is investigated and developed to meet the challenge of consistent and repeatable 3D structures from fsDLW, from design to characterisation. The formation of 3D PG structures with fsDLW is a stochastic process, therefore each structure formed from every writing instance would be unique in the arrangement of graphene flakes and pores. However, with consistent and repeatable fabrication conditions, the overall arrangement and properties of the 3D PG structures on the macro scale will have statistically similar results, such as similar pore sizes or a similar morphology of graphene flakes in PG. Solving these challenges will therefore enable optimisation of the 3D PG morphology without the need for individual control over the formation of each graphene flake.

Preparing MB and MSC designs for fsDLW

The effect of external variables on 3D structure formation is minimised by developing an overall process to fabricate and characterise the 3D PG structures formed from fsDLW, beginning with the overall design of the power source. The overall design of the 3D MBs and MSCs is just as important, if not more so than the 3D nanostructures formed. fsDLW is powerful as a means to rapidly write arbitrary patterns across a 2D surface. Therefore, in-plane designs such as interdigitated patterns are best placed to leverage on the strengths of fsDLW. Interdigitated patterns can be used for both MBs and MSCs; a separate process will be required to form the cathode for MBs, but the same 3D PG structure and material can be used for both electrodes in MSCs. Device design is not the focus of this research work, therefore deep consideration of the different design aspects of the interdigitated pattern, such as finger width or spacing will not be discussed.

The mechanically actuated galvano-scanner mirrors that allow for arbitrary patterning over a wide area are the source of both the greatest strengths and weaknesses of fsDLW. While these mirrors allow pulses to be rapidly scanned across the surface of any sample, the rapid rotation and movement of these mirrors are still subject to physics. When any movement is required, the corresponding galvano-scanner mirror must undergo acceleration and deceleration to reach the required velocity. Acceleration and deceleration at the edges of designs result in unevenness in amount of energy being exposed to material; a greater amount of energy is absorbed by the material near the edges of designs, leading to a lack of uniformity and control over the 3D structures formed at the edges [162].

To tackle the issue of uneven fluence arising from acceleration and deceleration of galvano-scanner mirrors, however, an additional design element, “wings”, are added to PG designs. While various methods have been developed to mitigate this effect, many of these methods are difficult and complex to implement. Instead, a simple alternative to mitigate this nonuniformity is to add a disconnected set of “wings” on either side of a design along the scanning direction. In this manner, acceleration and deceleration of the mirrors are limited to these disconnected wings, and the fluence across the important sections of the design remains uniform at constant scanning speed (v). Calculation of the minimum length of the wings, however, is not a simple task, as the conversion between angular and linear velocity rapidly becomes complex when considering speed changes through the f-theta lens. A much simpler, rule of thumb method is to observe the rough distance at which non-uniformity ends on either end of a straight written line. That point can then be assumed as the point when maximum velocity is reached, assuming acceleration and deceleration are the same. Therefore, by adding wings that are that distance apart (estimated to be 7 mm) (**Figure 3.3**) to either side of a design with a 2 mm gap,

the velocity across the design can be treated as constant. In this manner, the effect of uneven fluence from acceleration and deceleration can be minimised.

Verification of this method can be achieved by various means. The most straightforward is observation under optical microscopy to determine any visible changes across the PG pattern. However, these changes can be difficult to directly observe and quantify. Thermochromic paper could instead be used to verify this method. Thermochromic paper, or more commonly known as receipt paper changes colour when exposed to heating above a particular temperature (usually 348 K). By using a specific set of laser parameters (discussed in greater detail in **Chapter 4**), what is termed localised porous graphene (LPG) can be formed from PI adhered on to thermochromic paper without causing discolouration of thermochromic paper from excessive heating above 348 K. Critically, however, LPG formation depends on uniform fluence across a device pattern. If the fluence across the pattern is not even while writing, additional heating from the uneven fluence that is unaccounted for will cause discolouration of the thermochromic paper, as shown in **Figure 3.3(a)**. With the addition of wings, the fluence is kept even, and no discolouration of the thermochromic paper below will be observed (**Figure 3.3(b)**). In this manner, the usefulness of the wings can be verified. An example of wings is shown in **Figure 3.3(c)**. While this approach is not the most efficient in terms of time taken, the simplicity of the method works well enough for this research work. A more detailed discussion on how to implement these wings is covered in **Appendix A**.

With these considerations in mind, designs are drafted out in 2D or 3D modelling software, then exported as 2D vector file format such as “.dxf”. If required, grayscale images can also be written with the galvano-scanner, with fluence determined by saturation level of each pixel. The resolution of the images written is limited by the original resolution of the image and focal spot size. Image file formats such as “.jpeg” or “.png” can be directly used for writing. Files are then imported into the laser control software to be converted into line (vector) or raster (image) data that galvano-scanner controller can parse, and subsequently control galvano-scanner scanning mirrors to write the chosen designs into the material.

Choosing the precursor material

Choosing the appropriate precursor material for PG formation is the next step. In this research work, polyimide (PI) chosen because it is extensively used as an electronics substrate material. PI is also widely available commercially and is robust to thermal, chemical, and mechanical stresses at low cost [169, 170]. Together, these advantages render PG devices formed from PI more suitable for direct integration into smart wearables and IoT devices. Before writing, the surface of the PI film used is cleaned with ethanol to remove organic contaminants.

Figure 3.3. Controlling design uniformity and consistency in fsDLW. (a) Localised porous graphene (LPG) formation on thermochromic paper written without wings, causing uneven heating indicated by discolouration of the thermochromic paper. (b) LPG formation on thermochromic paper written with wings, resulting in even heating and no observed discolouration as expected. (c) PG formation without temporary adhesive PDMS layer below, causing wrinkles during patterning. Dotted area: Wing added to PG device design (d) PG formation with PDMS layer, without any wrinkling observed. (e) Repeatable calibration of height from the surface of the optical table to the top of the height gauge.

Preparing the precursor material for fsDLW

PI (or any other precursor material) is prepared for writing in the next step, where the main issue affecting reliability is the wrinkling of PI during PG formation. The formation of PG is a primarily photothermal process, where rapid heating of PI from intense laser irradiation causes the rapid carbonisation and graphitisation of the chosen precursor material [125]. Because writing is a serial process, heating induced by the laser will be uneven as the design is gradually written into the material. Depending on the form of PI used for device fabrication, the effect of wrinkling and curling can be vastly different. Generally, two types of PI are used in device fabrication in this research work. PI tape is usually used when the tape can directly adhere onto a substrate of interest before subsequent PG formation. During PG formation, the adhesive layer helps to reduce any curling or wrinkling by holding the PI film tightly and redistributing the thermal stresses throughout the adhesive layer. However, in instances where the adhesive is not required or might even actively impede integration (such when trying to transfer PG devices

from one substrate to another), PI film might be used instead. PI films, however, are highly susceptible to wrinkling, and care needs to be taken to mitigate this issue.

Without an adhesive holding down the film, uneven heating will lead to the formation of wrinkles or curls throughout the PI film (**Figure 3.3(c)**), resulting in unwanted changes in the effective beam area (and hence uneven fluence) as the beam is scanned across crests and troughs formed by the wrinkles and curls. As fluence is one of the main driving factors for the formation of PG, any uncontrolled variability would result in unwanted changes in the morphology of PG. However, uneven heating cannot be avoided owing to the serial nature of fsDLW. Instead, the PI film should be held down firmly onto a rigid substrate, so that heat-induced stresses that lead to curling can be absorbed and transferred away from the film during the writing process.

To tackle wrinkling and curling, a method to secure PI film or any other precursor material using PDMS as a temporary adhesive layer is developed. This temporary adhesion works to minimise the formation of wrinkles or curling of the precursor material during the formation of PG. Depending on the requirements of the device, PI tape (with a uniform adhesive on one surface) can be used to hold the film down evenly minimising curling or wrinkling during the writing. In cases where the use of PI tape is not ideal (such as when the film needs to be removed from the rigid substrate easily), scotch tape or masking tape could be as an alternative to hold down the sides of the film. However, wrinkling can still occur underneath in the central areas of the PI film where writing is done. Temporary adhesion of the film underneath the critical central areas of the film can be instead achieved by placing the film on a thick (1 mm) layer of PDMS drop casted onto a rigid substrate such as glass. Temporary adhesion is possible due to the high adhesive friction of drop casted PDMS, which most often manifests as a “stickiness” especially when two cured pieces of PDMS are in contact. The high adhesive friction allows PDMS to stick to many different materials, with relatively high shear and peel forces needed to separate PDMS from the other material. This method utilises the same property to hold precursor material down during writing, to minimise wrinkling. Thermal stresses will transfer to the PDMS layer while writing. In this manner, fluence can be kept uniform during the writing process. Removal of the PG written film can then be done by gently peeling the film off the PDMS. Examples of wrinkle reduction using this method are shown in **Figure 3.3(d)**, in comparison to securing the PI film at the sides using tape or without any securing at all **Figure 3.3(c)**.

Preparing the sample stage for fsDLW

Forming repeatable 3D structures in PI or any other precursor material requires a method to place the material within the scanning area below the galvano-scanner in a repeatable manner. The material need not be placed at the focal plane of the f-theta lens; depending on the fluence

required to form 3D MB and MSC structures, fluence can be tuned either by reducing pulse energy or by changing the beam area (focusing or defocusing). A means to repeatably determine the height of the f-theta focal plane from tabletop is therefore crucial. Instead of taking reference from the surface of the lens, focal height can be instead measured from the surface of the optical table using a height gauge. The height of the beam focus above the optical table is first determined empirically with pieces of thermochromic paper exposed to a stationary beam. Thermochromic paper changes colour when exposed to heat above a threshold temperature. The focal spot is found by exposing the surface of the thermochromic paper with a few pulses at high repetition rates and slowly raising or lowering the height of the sample stage towards the expected position of the focal spot. Pulse energy is steadily reduced while stage height is changed such that discolouration of the thermochromic paper (with sufficient photothermal heating) can only occur at the focal point. With the focal point (and thus focal plane) identified, the precursor material can be placed repeatably at that height using a height gauge (**Figure 3.3(e)**), and any additional defocusing can be measured relative to the focal plane height. In this manner, PI and other precursor materials can be repeatably written to form 3D structures across a large area.

Choosing laser and process parameters

Once the cleaned and secured precursor material is placed at or a required distance away from the focal plane, writing can begin. Laser and processes parameters can be chosen, appropriate to the imported vector or image designs in the laser control software. Depending on the writing mode, different process parameters are made available, but laser parameters such as fluence, repetition rate and the number of pulses remain common. Different 3D structures can be formed across the overall design depending on the writing mode chosen. In the scanning mode, process parameters are scanning speed, hatch spacing and scanning strategy among others. Scanning of the laser beam along paths determined by the design results in the formation of 3D PG along those paths when optimal parameters are chosen. Dot spacing and dwell time for each dot can be controlled by the laser for raster mode. The raster mode is used with images, where images are drawn by a combination of dots instead of solid lines. Taken as a whole, these dots combine form pictures. The overall effect of rastering is akin to multiple single spot exposures rather than continuous line writing, but rastering is still considered under the umbrella of fsDLW. Depending on the effect and type of 3D structure required, either rastering or scanning can be chosen for the same overall design. While process and laser parameters are treated separately in the control software, the effects of both on the formation of 3D PG structures are strongly related. Many of these parameters play major roles in how 3D structures are formed, primarily due to how they affect the spatial and temporal profile of energy deposited into the material. A more in-depth investigation into how these laser and process parameters utilised to form 3D PG

structures for MBs and MSCs will be discussed in **Chapter 4**. Once all parameters are carefully chosen, laser marking can begin, and the 3D structures are directly carbonised and graphitised out of the PI. Examples are shown in **Figure 3.4**, such as a PG 3D MB anode assembled with a copper current collector (**Figure 3.4(b)**), logos of Panasonic and Nanyang Technology University written as PG to showcase the flexibility of the patterning process (**Figure 3.4(c)**), integrated PG MSC and humidity sensors (**Figure 3.4(d)**) and PG pressure sensors (**Figure 3.4(e)**). Some of these applications and examples will be discussed in further detail in the later chapters.

Characterising 3D PG structures formed

The final step in the fsDLW PG process is to characterise any structures formed; in terms of morphology (3D structure) and chemical composition which is especially important since the PG structures are expected to contribute directly to power storage for both MBs and MSCs. Morphology is characterised from optical characterisation as well as through field emission scanning electron microscopy (FESEM). Features such as the size of pores formed on graphene flakes as well as overall arrangement of flakes are investigated to get an understanding of how 3D arrangement could contribute to MB and MSC performance. Chemical composition, which contributes to MB and MSC performance is characterised through Raman spectroscopy. By comparing the intensity ratio of specific peaks measured, PG can be compared to graphene in terms of chemical composition. This composition can then be quantitatively linked to MB and MSC performance. If characterisation results are not satisfactory, the process is repeated at different parameters (with different designs if necessary) to further improve the PG formed. In this manner, a wide range of structures can be identified and characterised, and the performance of each related to 3D MBs and MSCs.

Further optimisation and testing can be achieved by testing the electrical performance of devices as MBs and MSCs either through half-cell for lithium-ion MBs or by depositing electrolyte onto the fingers of the interdigitated pattern and measuring capacitance values through cyclic voltammetry (CV). By integrating materials dispensing or packaging and current collector materials, further fabrication of full MBs and MSCs can be achieved, which will be discussed in a later section. An overview of the methodology is presented in **Figure 3.4(a)**.

If more control is required over the 3D structures formed fsLIL should be used instead. In the next section, research and development of the fsLIL set-up for 3D structuring will be investigated in greater detail.

Figure 3.4. fsDLW methodology and examples. (a) Overview of the fsDLW methodology for consistent and reliable patterns. (b) Assembled PG anode with a copper current collector for lithium-ion MBs. (c) Logos for Nanyang Technological University and Panasonic written in PG. (d) PG MSC (left) and humidity sensor (right) for integrated graphene-paper electronics. (e) PG pressure sensors written with wings.

3.4 3D material structuring on the femtosecond laser interference lithography (fsLIL) platform

fsLIL is a complementary process to fsDLW that can be used to directly form 3D periodic patterns in different MB and MSC materials instead of through multiple complex photolithographic steps. Laser interference patterns in a wide variety of configurations have been used to develop complex patterns at high aspect. Subsequent MB and MSC materials can then be deposited onto these high aspect ratio 3D structures to form surface-conformal 3D MBs and MSCs. When the indexing mount is replaced, pulses leaving the half-wave plate is instead redirected towards the fsLIL interference set-up. Instead of using a lens like in the fsDLW set-up, beam size in the fsLIL set-up is controlled using a beam expander placed before the beam

splitter. Use of a beam expander helps to maintain temporal coherence after beam splitting and ease of calibration. Depending on the 3D pattern required, the pulses are then split into any number of paths and then redirected towards a common interference plane. The challenge, however, is to overcome the low temporal coherence of femtosecond pulses such that superposition at the common interference plane can still occur while still maintaining enough fluence to direct pattern materials [31].

To that end, there is a need to research and develop a femtosecond interference set-up that can maintain pulse coherence along beam paths while still flexible enough to create a large variety of periodic structures. The set-up must also have a simple means to determine pulse interference. The developed interference set-up and schematic are shown in **Figure 3.5**.

Figure 3.5. fsLIL set-up. (a) Image of the overall fsLIL set-up, with a beam splitter and plate compensator on the left under the brown shelf, angle control in the middle, and sample stage on the right of the image. (b) Schematic of the overall fsLIL set-up, with the reflected beam in purple, and un-reflected beam in blue. M: Mirror, BS: Plate beam splitter, PC: Plate compensator, θ : Interference angle. (c) Intersecting beam paths, revealing the position of the interference plane.

3.4.1 Beam splitting and interference optics – development, configuration & control

The main challenge that the fsLIL set-up needs to overcome is maintaining and ensuring the coherence of pulses along different beam paths to interfere at the interference plane. Femtosecond pulses consist of many overlapping modes in superposition to form the sharp intense pulse, which results in a large bandwidth ($\Delta\nu$) compared to picosecond pulses. From the coherence equation: $L_c = c\tau_c = c/\pi\Delta\nu$, this large bandwidth results in a low coherence length. Coherence length effectively dictates the maximum optical path difference (OPD) between two or more beams for interference. Therefore, the design of the fsLIL set-up needs take into consideration so that $OPD < L_{coh}$. For the majority of this research work, the simpler two-beam set-up will be designed and developed.

Pulse splitting

The first thing to take into consideration when designing a fsLIL setup is in how femtosecond pulses are split. Pulses must be split with minimal difference in path length after splitting while allowing high fluence. Path beam splitting with low path difference can be achieved with a plate beam splitter in combination with a compensation plate. In laser-based imaging, pellicle beam splitters are used to minimise back-reflections and any other imaging artefacts that could degrade image quality, which is essential to minimising OPD. However, pellicle beam-splitters are fragile; high-intensity pulses from femtosecond lasers would immediately damage and burn such beam splitters, especially at fluences high enough to pattern materials. Beam splitters made of sturdier materials such as quartz must be used to mitigate damage at high fluence instead. Using a plate beam splitter helps mitigate issues with high fluence, with the drawback of requiring an additional compensator plate in the reflected path to account for the OPD from the thickness of the plate splitter and greater energy loss due to pulse absorption in the material. However, these drawbacks can be mitigated at higher fluences. The plate beam splitter is mounted on a kinematic mount to ensure a full range of adjustability. The contrast in the interference patterns is maximised by using a half-wave plate before the plate splitter. Beam splitting for high fluence patterning can therefore be achieved with a plate beam splitter (**Figure 3.5(b)**).

Controlling interference angle

The next consideration in controlling OPD is in how the angle of interference is controlled. Direct patterning requires a set-up that offers the most amount of flexibility and fluence for direct patterning. To meet this challenge, a modified two-beam set-up is developed, where four additional mirrors are added into the standard mirror-based diamond two-beam set-up. In the

simplest case of two-beam interference, the angle of interference (θ) directly affects the pitch of interference pattern formed (Λ) from $\Lambda = \lambda/2 \sin \theta$. Therefore, changing the interference angle through the set-up must be simple to be able to flexibly form a range of patterns, while still maintaining high enough fluence for direct patterning. With fixed angle Wollaston prisms, alignment might be simplified, but the loss in control over the interference angle makes it unlikely to form a wide range of patterns with such prisms. Power losses with transmission through these prisms is another drawback. With a mirror-based system in comparison, a greater amount of flexibility with reduced power loss is possible, which is critical for direct patterning. The simplest diamond-shaped set-up consists of two mirrors rotated at equal angles but in opposite directions, which allows for flexible patterning over a wide range of angles. However, at narrower interference angles ($< 10^\circ$) which are essential for the larger pitch sizes ($< 1 \mu\text{m}$) for 3D MBs and MSCs (as discussed in **Chapter 2**), the simple mirror set-up is insufficient, as the elliptical width of the beam when striking the mirror exceeds the limited width of the laser mirrors (often 25.4 mm in diameter), causing a significant section of the beam to not be reflected. To mitigate this issue, four additional mirrors are added into the beam set-up such that the angle of the incoming beams is reduced for the same interference angle, as shown in **Figure 3.5(b)**. These mirrors thereby ensure that the elliptical widths of the incoming beams are reduced to fit within the width of the mirror at smaller interference angles while maintaining the overall flexibility of the set-up.

Optical path calibration

Calibration of the fsLIL set-up to ensure that the arriving pulses are within the coherence length is the third consideration. A simple method is developed to quickly calibrate the path delay to minimise the need to check via direct patterning. A schematic of the calibration set-up is shown in **Figure 3.6(a)**. A thin (200 μm thick) glass slide attached onto a kinematic mirror mount is placed directly opposite of the plate beam splitter at the sample plane (**Figure 3.6(b)**). A second glass slide is added to one of the paths to account for the additional path length delay. The thin glass slide acts in the opposite manner of the plate beam splitter, allowing the two beams to recombine along two almost parallel paths for interference fringes at the glass beam splitter to form. The mirror mount is attached to a removable indexing mount for easy replacement and removal. These fringes are then projected on a screen or wall behind the set-up, with the use of a diverging lens. By monitoring the orientation and relative brightness of the projected fringes, the alignment of the beam paths can then be adjusted. Properly adjusted beam paths will form interference fringes that are clear and vertically aligned; any skew in the beam paths out of the plane will result in tilting or bowing of the fringes instead. Next, the brightest set of fringes need to be identified to determine if the OPD is less than the coherence length. As the path length in one arm is changed (keeping angles constant), the brightness of the observed fringes

changes. Several distinct sets of fringes can be identified around a central bright set of fringes with the distance between dark fringes proportional to the width of the beams, akin to interference patterns formed from two-beam interferometry with a diffraction envelope. As OPD approaches zero, the overlap of the two beams increases before decreasing again as OPD increases again. When the two beams are at maximum overlap at the glass beam splitter, the coherence condition for fsLIL is met ($OPD < L_c$). For instances where the difference in brightness is minimal, the middle set of bright fringes can be taken to be the central set of fringes. Therefore, the coherence condition for OPD can be met by identifying the central set of fringes through this simple method.

Once calibration is complete, the glass beam splitter can be removed from the indexing mount. Samples can then be placed at the interference plane on the sample stage for direct patterning, which will be discussed in **Chapter 6**.

Figure 3.6. Optical path calibration set-up and results. (a) Schematic of calibration set-up (dotted lines) arranged in the overall fsLIL set-up. M: Mirror. (b) Calibration beam splitter on a removable index mount at the interference plane. (c) Projected fringes of a properly calibrated fsLIL set-up. (d) Projected fringes of a poorly calibrated fsLIL set-up.

Characterisation of 3D structures

For greater design flexibility, a four-beam variant is undergoing active development for fsLIL (**Figure 3.7**). Beam splitting with equal pulse intensity and minimal OPD is achieved with custom-designed interference gratings from Ibsen Photonics for each wavelength (**Figure 3.7(b)**). The grating is designed such that more than 90% of the incoming energy of the pulses are split equally between the zeroth and first-order beams, with all pulses linearly polarised to 45° . The angle of diffraction for the first-order beams is 51.84° . The overall set-up is designed with the same considerations in mind, with calibration achieved with one beam pair at a time. To reduce the complexity of the set-up (at the cost of smaller interference angles), a simple “umbrella” design is used with four mirrors each directing the diffracted first order beams towards a common interference plane. Further work needs to be done to calibrate and utilise the set-up as required for 3D patterning.

With the fsLIL set-up developed, the process for fabricating 3D structures for MBs and MSCs can be discussed further.

Figure 3.7. Four-beam fsLIL set-up. (a) Schematic of the umbrella-type four-beam fsLIL set-up with gimballed mirrors. (b) Phase grating for 515 nm. Similar phase gratings for 343 nm and 1030 nm are also available. (c) Assembled four-beam set-up for further calibration and set-up.

3.4.2 fsLIL patterning process for 3D periodic structures

The process for fabrication first begins with determining the required periodic pattern, and the subsequent process and laser parameters (such as interference angle and polarisation angle) for the pattern (**Figure 3.8**). The number of patterns is limited with two beams, but parameters can be simply determined from the interference equation introduced before. A more general (and complex) form of the interference equation for multiple beams is used for three or more beams, with a correspondingly greater number of patterns able to be formed, as discussed in the

literature review. In this research work, however, the two-beam set-up for fsLIL is sufficient as pattern design is not the focus of research work in this thesis. Laser parameters are also determined at this step, depending on the optical properties of the material to be patterned. The interference set-up and laser controls can then be adjusted as needed. Once set-up is complete and calibration of path lengths complete as discussed, patterning can then be done with the required laser and process parameters.

Characterisation of the fabricated 3D structures is done with laser confocal microscope and SEM, to determine how well the fabricated structures match the expected periodic structures. Various aspects of surface area, such as AEF and aspect ratio of the patterns can then be determined and optimised with more experiments. Active MB or MSC materials can then be subsequently deposited onto the fsLIL 3D structures to form 3D MBs and MSCs, for further characterisation of storage performance. An overview of the fsLIL methodology and examples of patterned materials are shown in **Figure 3.8**.

An example of 3D structures directly patterned in a material is shown in **Figure 3.8(b)**. These 3D structures come in the form of Volume Phase Gratings (VPGs) directly patterned into polydimethylsiloxane (PDMS), an optically transparent and stretchable elastomer using the developed fsLIL set-up. Each of these VPGs are 3D in nature, essentially formed out of a periodic 1D array of stacked 2D planes which diffracts light passing through. These planes are formed from areas of altered refractive index and can then be subsequently used in beam steering and tuneable spectroscopic applications. Other examples of directly patterned substrates are shown in **Figure 3.8(c) & (d)**, where the fsLIL set-up is used to pattern AZ9260 photoresist. 1D periodic arrays with a pitch of $1.28\ \mu\text{m}$ (from a theoretically calculated pitch of $1.37\ \mu\text{m}$) are formed with an aspect ratio of 3:1 aspect ratio. These patterns are fabricated to study the effect of beam expansion for fsLIL, where fsLIL patterning across the width of two expanded interfering beams is found to be spatially limited by the coherence of the interfering pulses. Some of these examples and applications will be discussed in greater detail in the following chapters.

Figure 3.8. fsLIL methodology and examples. (a) Overview of the fsLIL methodology for direct periodic patterning of materials. (b) Direct patterning of optically transparent and stretchable PDMS substrates to form volume phase gratings (VPGs). (c) Direct patterning of AZ 9260 photoresist. (d) 50X confocal image of patterned AZ 9260 photoresist.

3.5 Summary

In this chapter, methods, instrumentation, and set-ups to reliably form 3D structures using fsDLW and fsLIL were investigated and discussed. First, an in-line set-up and method to monitor repetition rate, number of pulses and fluence during fabrication to improve process reliability was developed.

Next, methods to improve the process reliability of fsDLW to form and characterise 3D PG structures from PI were developed and demonstrated. This method consisted of several steps. At the first step, a method to reduce uneven fluence distribution was achieved by adding additional design elements termed “wings” in the design along the expected direction of scanning, such that acceleration and deceleration of the mirrors occur within the wings only. In the next step, this model was then converted into process parameters by the laser control software. Process and laser parameters were chosen specifically for the material such that PG was formed in an optimised and usable manner. In the sample preparation step, a method was

developed to secure PI and other precursor materials for fsDLW with a combination of tape and a thin layer of PDMS below. In effect, the layer of PDMS was used as a temporary adhesive to reduce wrinkling from uneven heating during the writing process, leveraging on the high adhesive friction of PDMS's surface. In the last step before patterning a method to ensure consistent positioning of PI samples in the z-direction was developed. PG structures could then be fabricated with fsDLW. Lastly, characterisation of PG structures was achieved through a combination of Raman spectroscopy, which was used to investigate the chemical composition of the graphene, and laser confocal and SEM, which was used to investigate the morphology of the PG structure formed. The whole process together ensured that the 3D PG structures could be reliably and repeatably formed. Development of this process enabled the investigative study on PG formation in **Chapter 4** and **Chapter 5**.

In the following section, the design and development of the fsLIL set-up for direct patterning of substrate materials for 3D MBs and MSCs was investigated in detail. Due to the low temporal coherence of femtosecond pulses and high fluence requirement for patterning, special considerations had to be accounted for in all parts of the interference set-up. Development began with determining the beam splitting method, where a plate beam splitter was chosen to allow high fluence patterning. Next, the standard two-beam set-up was improved with additional mirrors to enable interference patterning at smaller interference angles. To ensure that optical path calibration could be done quickly with the developed set-up, a simple method was developed to quickly ensure that OPD is kept within the coherence length for interference. Based on the same principles, a four-beam umbrella set-up was also developed for future research. In combination with the two-beam set-up, a process to directly pattern materials with fsLIL was developed and later used to pattern 3D structures into various substrates. Results of this study are detailed in **Chapter 6**.

The work presented in this chapter is envisaged to further the development of fsDLW and fsLIL for fabricating 3D MBs and MSCs reliably and consistently.

Chapter 4: Theoretical modelling and experimental validation of femtosecond direct laser writing (fsDLW) for porous graphene (PG) micro-batteries (MB)

A method to easily predict porous graphene (PG) formation from femtosecond direct laser writing (fsDLW) will be a powerful tool to determine optimal conditions required to form PG. This chapter will begin with the background and motivation for the analytical approach chosen, followed by the formulation of the temperature model to predict the temperature rise across the surface of polyimide (PI) with laser irradiation. Experimental verification follows the completion of the model, with characterisation of the PG formed and the differences between predictions and the actual formation of PG. Insights into the formation mechanisms of PG will then be discussed, and the chapter will end with a demonstration of PG used as a 3D lithium-ion MB anode.

4.1 Introduction

Porous graphene (PG) is a networked, porous 3D arrangement of graphene flakes that can be formed from femtosecond direct laser writing (fsDLW). The combination of a large, 3D surface area, low permittivity (for higher capacitance), high energy capacity and high electrical conductivity to function as a current collector makes PG potentially useful as electrodes for both 3D MBs and MSCs [147, 148].

Much work has gone into understanding the structures and morphology of PG formed, from the formation of fibrous structures to open sheets, each of which plays different roles in possibly enhancing the storage potential of 3D MCs and MSCs [149, 164]. Despite the increasing amount of research into the mechanisms of PG formation, an analytical method to predict and optimise the formation of PG is still lacking [171-173]. Experimental validation of this model will also lead to further insights into the formation of PG, especially where PG formation diverges from prediction.

Theoretical modelling and simulation is a powerful approach to establish a greater understanding of the basic physical processes that underlie PG formation and enable prediction. By modelling the basic principles of PG formation, such as photothermally driven carbonisation and graphitisation, greater insights can be drawn and otherwise hidden mechanisms and

mechanistic interplays during the formation of PG can be revealed [125]. From these mechanisms, optimal conditions for PG formation can be derived.

Various theoretical approaches have been taken to identify some of these mechanisms. Approaches can be categorised into numerical methods, based on useful approximation versus real analysis based on analytical formulations. Numerical methods such as molecular dynamic (MD) simulations are a useful tool to investigate the chemical changes during the carbonisation and graphitisation process, by modelling the interactions of atoms and molecules on each other via a numerical method. Using MD simulations, various useful insights, such as the impact of the precursor polymer on the quality of PG formed, or the impact of pressure on the formation of layered graphene clusters, among others, can be discovered [172, 174, 175]. Other models, solved using other numerical methods such as finite element analysis (FEA) were used to determine the temperature distribution within PI for carbonisation [173]. However, while results based on numerical methods can provide useful and important insights into formation mechanisms, such methods are difficult to replicate and reproduce without full knowledge of the simulation conditions used and are often computationally expensive to implement. Analytical methods, which are derived from basic physical concepts and formulas in contrast are much easier to utilise for other researchers. The same implementation of equations will lead to the same results without any approximation inherent in numerical methods and without the need for computationally expensive implementations.

The main challenge is therefore to develop an analytical formulation that can predict the formation of PG. This formulation needs to consider two aspects: heating in PI from pulsed laser irradiation, and the carbonisation and graphitisation process from heating, since PG formation is mostly driven by photothermal heating. A significant amount of research has been focused on heating is accumulated in different materials with pulsed lasers and laser carbonisation of PI [176-178]. However, these studies alone do not enable the prediction of PG formation. What is missing is a model that is able to capture the whole process from irradiation to graphitisation.

The challenge of predicting PG formation is achieved with an analytical temperature model developed in combination with a simple temperature boundary. The developed temperature model incorporates temperature-dependent laser and material parameters to model the temperature distribution across the surface of PI with different fsDLW laser parameters. The formation of PG from different laser parameters can thus be predicted by taking a temperature boundary ($T_{grphtn} = 1775$ K) as a proxy for the formation of PG, these predictions are then validated by irradiating PI using the same femtosecond UV laser system described in **Chapter 3**. Validation shows that when the predicted temperature from laser irradiation is above T_{grphtn} ,

the formation of PG is observed. This validation thereby lends further evidence to the overall hypothesis of PG formation being largely driven photothermally. Further analysis of the formation mechanisms of PG reveals with a distinct stable amorphous carbon (a-C) transition state at temperatures below T_{grphn} which is formed from carbonisation without subsequent graphitisation. 3D PG anodes are fabricated and characterised in lithium-ion MBs to demonstrate the potential of PG in 3D MBs. These insights can be envisaged to further the development and optimisation of PG formation from fsDLW. The temperature model discussed in this chapter will also provide a useful tool for other researchers to predict parameters for forming PG for different ultrashort laser and material systems.

4.2 Modelling laser and material parameters for thermally localised laser graphitisation (LLG) with femtosecond direct laser writing (fsDLW)

4.2.1 Theoretical formulation of fsDLW laser-material interaction

The first step in the development of the analytical model is to define the region of interest. The region of interest as shown in **Figure 4.1** is the top surface of a two-layer tape system with a 25 μm PI layer followed by a 40 μm of silicone adhesive (compressed from 70 μm through adhesion) to make up a total of 65 μm of PI tape adhered onto a glass substrate. The time and space-dependent temperature distribution $T(\vec{r}, t)$ inside both PI and the adhesive layer can be obtained from the thermal diffusion equation given by **Equation (4.1)** [179]:

$$\nabla^2 T(\vec{r}, t) - \frac{1}{D} \frac{\partial T(\vec{r}, t)}{\partial t} = f(\vec{r}, t) \quad (4.1)$$

Here $f(\vec{r}, t)$ is the rate of change of heating inside the medium defined (**Equation (4.2)**) as the time derivative of generated heat density ($Q_{laser}(\vec{r}, t)$). Femtosecond pulses impinging the surface of PI first rapidly excite electrons within the duration of the pulse, before energy from these excited electrons are transferred to the lattice over a longer timescale. For PI, the rate of conversion of electronic to heat (vibrational) energy occurs roughly at 30-40 ps [180]. Comparatively, the time it takes for the generated heat to diffuse along one absorption length ($1/\alpha$) of PI ($D \approx 10^{-7} \text{ m}^2 \text{ s}^{-1}$) is calculated (diffusion length $= \sqrt{4Dt}$) to be 50 μs . Therefore, it takes a significantly longer (6 orders of magnitude) time duration for the heat to diffuse away than for heat to be generated. Consequently, generation of heat via the transfer of energy from excited electrons to the lattice results in swift heating upwards of 10^{14} K s^{-1} [107]. The time dependency of the source term $f(\vec{r}, t)$ can thus be described by a femtosecond pulse having

Dirac delta time function, $\delta(t)$. By considering the Gaussian transverse spatial distribution and other related parameters, the source term can be written as follows in **Equation (4.2)**:

$$f(\vec{r}, t) = -\frac{1}{\rho C_p D} \left[\frac{\partial Q_{laser}(\vec{r}, t)}{\partial t} \right] = -\frac{1}{\rho C_p D} \left[\alpha(1-R)F e^{-\alpha z} e^{-\left(\frac{2r^2}{\omega_{theo}^2}\right)} \delta(t) \right] \quad (4.2)$$

Here r is the radial distance from the centre of the focal spot and ω_{theo} is the focal spot radius that follows the Gaussian beam propagation (**Equation (4.3)**).

$$\omega_{theo} = \omega_0 \left\{ 1 + \left[\frac{\lambda z}{\pi \omega_0^2} \right]^2 \right\}^{1/2} \quad (4.3)$$

The pre-exponential term in **Equation (4.3)** contains information about the material properties of both materials, such as density (ρ), specific heat capacity (C_p), reflectivity (R), absorption coefficient (α) and thermal diffusivity (D). The temperature raised due to a single femtosecond pulse is obtained by solving the heat equation (**Equation (4.1)**) with the source term given in **Equation (4.3)**. The solution at the surface ($z = 0$) can be obtained using Green's function method with initial conditions $T(\vec{r}, 0) = 300$ K in **Equation (4.4)** [181]:

$$T_1(r, z, t) = \frac{T_{peak}}{2\sqrt{\pi}(1+\tau)} \exp \left[-\frac{2r^2}{\omega_{theo}^2(1+\tau)} \right] T_z(z, t) \quad (4.4)$$

Here, $T_{peak} = (\alpha(1-R)F)/(\rho C_p)$ is the pre-exponential term from **Equation (4.2)** and describes the instantaneous peak temperature due to the femtosecond pulses. The term $\tau = 4Dt/\omega_{theo}^2$ in the denominator determines the rate of heat diffusion along the radial and axial directions. Energy absorption and thermal diffusion processes can be treated as separate events in the femtosecond pulse regime, as the laser pulse duration is very short compared to the electron-lattice coupling time [182, 183]. The absorbed energy is then assumed to be converted into thermal energy describable by Boltzmann statistics immediately after absorption [184]. In this regime, the longitudinal (z) distribution of temperature along the depth (z) of the sample can be prescribed by exponential decay function $e^{-\alpha z}$, where α is the linear absorption coefficient of the material under consideration (**Figure 4.1(a)**) [182-184]. Considering this initial exponential decaying function, the longitudinal part of temperature distribution after the inclusion of thermal diffusion in PI can be written as in **Equation (4.5)** [182, 184]:

$$T_z(z, t) = \exp(\alpha^2 Dt) \left[e^{-\alpha z} \operatorname{erfc} \left(\alpha(Dt)^{1/2} - \frac{z}{2(Dt)^{1/2}} \right) + e^{\alpha z} \operatorname{erfc} \left(\alpha(Dt)^{1/2} + \frac{z}{2(Dt)^{1/2}} \right) \right] \quad (4.5)$$

Heat generation and diffusion within the PI and adhesive layers differ based on the material properties of both materials accordingly. Therefore, the combination of heat generation and

diffusion in the two-layered medium results in the overall temperature distribution $T(\vec{r}, t)$ for a single pulse. During the formulation of femtosecond pulse induced temperature increment in PI and the silicone adhesive, several assumptions have been taken into consideration. First, the bond dissociation energies for ground electronic states in PI can be estimated to range from 5 eV to greater than 8 eV. Thus, the major contribution in the material modification is by the photothermal mechanism, although the photochemical process cannot be ruled out completely [185]. Secondly, multiphoton processes are ignored, since the excited states are expected to last of the order of tens of picoseconds for PI [184]. Third, during the laser irradiation, any radiation loss and plasma effect have been neglected [173]. Fourth, PI is assumed to transition through an intermediate a-C stage during the transformation into PG [186]. Fifth, the absorption coefficient (α), reflectivity (R) and density (ρ) of PI is assumed to have no strong temperature dependence, and are similar to that of subsequently formed a-C and PG [180, 187, 188]. Sixth, the optical properties of the silicone adhesive layer between PI and the glass substrate are not considered in the thermal model. Lastly, thermal accumulation modelling is assumed to be performed on a heated, but non-ablated PI surface for simplicity [180].

To identify the conditions for PG formation, a temperature boundary needs to be established at the surface of the PI tape. The first boundary for the top surface of the PI describes the minimum temperature threshold for the formation of PG. It has been reported that, for conventional isothermal heating of Kapton films, degradation occurs upon heating above approximately 850 K in ambient conditions to form a-C with a low to a minimal degree of graphitisation [189]. Temperatures higher than 1775 K are required to promote thermal graphitisation, leading to the formation of PG [177]. Effectively, the temperature can be taken as a proxy to predict the formation of PG. Therefore, 1775 K can be taken as a temperature threshold (T_{grphn}) to determine the formation of PG.

The reflectivity (R) and absorption coefficient (α) of the PI film at 343 nm are measured using an integrating sphere and found to be 0.082 and $2.1246 \times 10^5 \text{ m}^{-1}$ respectively. The density of the PI film is taken to be $1.42 \times 10^3 \text{ kg m}^{-3}$ [190]. The only temperature-dependent parameter considered in the modelling is the thermal diffusivity (D) which depends on thermal conductivity (κ) and specific heat capacity (C_p) through the relation, $D = \kappa/(\rho C_p)$. The temperature dependency of C_p and κ is taken stepwise to account for material changes from PI to PG occurred due to heat accumulation. Between 300 K – 858 K, $C_p(T)$ and $\kappa(T)$ is adopted from the reported empirical expression, beyond which carbonisation is reported to begin [173, 180]. Beyond 858 K, the complete formation of a-C and subsequently graphene is assumed, and $C_p(T)$ is taken to be constant, as both a-C and graphene C_p share similar C_p values at 858 K [191, 192]. Following similar reasoning, $\kappa(T)$ is taken to be constant for $858 \text{ K} < T < 1775$

K [193]. At and above 1775 K, PI is assumed to be fully converted to PG, and κ is taken to be $0.7 \text{ W m}^{-1} \text{ K}^{-1}$ based on reported values for similar PG [194]. These conditions are summarised as follows:

$$c_p(T) = \begin{cases} 1000 \left[0.96 + 1.39 \left(\frac{T-300}{400} \right) - 0.43 \left(\frac{T-300}{400} \right)^2 \right] & \text{if } 300 \text{ K} \leq T < 858 \text{ K} \\ c_p(T) & \text{if } T \leq 858 \text{ K} \end{cases} \quad (4.6)$$

$$\kappa(T) = \begin{cases} 100 \times \left[(1.55 \times 10^{-3}) + (6 \times 10^{-4}) \left(\frac{T-300}{400} \right) - (1.7 \times 10^{-4}) \left(\frac{T-300}{400} \right)^2 \right] & \text{if } 300 \text{ K} \leq T < 858 \text{ K} \\ \kappa(T) & \text{if } 858 \text{ K} \leq T < 1775 \text{ K} \\ 0.7 & \text{if } T \leq 1775 \text{ K} \end{cases} \quad (4.7)$$

Figure 4.1. Modelling and prediction of temperature from femtosecond pulses. (a) Schematic of the modelled region in the PI film within which focused femtosecond pulses induce a temperature distribution ($T(\vec{r}, t)$). (b) Predicted temperature rise due to a single femtosecond pulse at different F values with temperature rise omitted for clarity. Inset: Schematic of temperature rise (T_{rise}) due to one pulse and diffusion time (τ_d) after peak temperature rise. (c) Predicted temperature rise across 5.0 ms due to different N pulses with different repetition rates (f) or periods (τ_L) at the same fluence ($F = 0.034 \text{ J cm}^{-2}$). Inset: Schematic of temperature accumulation (T_{accum}) due to multiple pulses.

For simplicity, no temperature-dependent material properties are considered for the silicone adhesive, and the thermal conductivity of the silicone adhesive is taken to be similar to PI without heating [195]. By considering the material properties of PI, the temperature-rise and subsequent temperature distribution due to a single pulse can then be determined for different fluences, as described in **Figure 4.1(b)**. When considering a train of femtosecond pulses with a repetition rate (f), heat is generated at time intervals of $t_L = 1/f$. The temperature profile is modified each time a new laser heating pulse arrives, by an instantaneous temperature rise (T_1). Thus, the temperature rise due to N number of pulses can be written by a summation of temperatures by each pulse (n) that depends on the repetition rate $1/t_L$ as follows [179, 196, 197].

$$T = T_{amb} + \sum_{n=0}^{N-1} [T_1(t - nt_L)H(t - nt_L)] \quad (4.8)$$

Here, $T_{amb} = 300$ K, the ambient temperature and $H(t - nt_L)$ is the Heaviside function which ensures that the pulses that have not reached the surface at the time of consideration (t) do not affect the thermal accumulation. During thermal accumulation, the temperature effect from the previous pulse is considered through the temperature dependence of C_p and κ using **Equations (4.6) & (4.7)**. The final temperature T is taken at the point of maximum heating from the last pulse. Temperature accumulation due to multiple pulses can then be predicted at varying repetition rates f , number of pulses N and fluence F , as shown in **Figure 4.1(c)**. From **Equation (4.8)**, it follows that a larger N will need a smaller F to reach the same temperature and vice versa. Implementation of this theoretical formulation in MatLab® code is detailed in **Appendix B**.

4.3 Experimental validation for PG formation

4.3.1 Materials & methods

Material preparation

PI tape (3M Electrical Tape Series 92) consisting of a $23 \mu\text{m}$ thick layer of PI film on a $60 \mu\text{m}$ thick silicone adhesive layer (measured directly using a micrometre screw gauge) is used as the precursor and substrate for femtosecond PG formation. The PI tape is directly affixed on a rigid glass slide 1 mm thick. Before writing, the surface of the PI film is cleaned with ethanol to remove organic contaminants.

Femtosecond direct laser writing of PI

Femtosecond pulses are focused onto the surface of the PI tape using a THG (343 nm) femtosecond laser galvano-scanner set-up (Fig. 1f) to modify the PI at different spots, each with

different fluence (F from 0.023 J cm^{-2} to 0.068 J cm^{-2}), repetition rates (f from 50 to 500 kHz), and the number of pulses (N from 1 to 5,000). Writing on the PI tape samples is done through the fsDLW writing system described in **Chapter 3**. Femtosecond pulses are focused on to the surface of the PI tape (adjustable via a manual x-y-z-stage). Control of the focal position in the x-y plane is achieved through a computer-controlled galvano-scanner (Sino-Galvo JD2204 Galvo Scanner) fitted with a f-theta lens (Sino-Galvo f-theta lens) with 160 mm focal length. The beam waist ω_{theo} ($47 \mu\text{m}$) is measured directly using the knife-edge method. The laser used is a linearly polarised Yb-fiber femtosecond laser (Amplitude Systemes Satsuma HP) with a 220 fs pulse duration (τ_p) and adjustable f from single shot to 2 MHz. The third harmonic (THG) wavelength (343 nm) is used for fsDLW, to maximise single-photon absorption for PI, which is highly absorbing in the UV spectrum [198]. All writing is done under ambient conditions.

To verify whether these same PG parameters can be used to form arbitrarily shaped PG devices, these PG spot parameters are translated into equivalent scanning parameters. A simple scanning strategy is used, where the number of pulses incident on single spot N is treated as equivalent to N pulses across the theoretical beam diameter ($\omega_{theo} = 46 \mu\text{m}$). In this manner, N can be translated to N per mm, which is further translated to an equivalent scan speed based on f . F and f are taken to be the same. Scanning parameters are rounded to the nearest multiple of 25 for simplicity. Single lines are written by the galvano-scanner in this manner. 2D shapes are then formed by overlapping multiple lines perpendicular to the scanning direction with an overlap of 33% of ω_{theo} . Lines are written in a single direction to minimise heat build-up at corners. Wings are added to written patterns to minimise the effect of uneven fluence from acceleration and deceleration of the galvano-scanner mirrors as discussed in **Chapter 3**.

Material characterisation

After writing, Raman spectroscopy is employed to study any material changes such as the formation of PG at the irradiated spots (spot PG) and to identify the characteristics of the PG and other carbonaceous materials formed both from single spots and the larger devices formed. Raman spectra (Renishaw InVia Raman microscope) are obtained by exciting the written carbon materials using a 633 nm laser at 100X magnification (unless otherwise stated), and peak positions and widths are obtained from peak fitting with OriginLabs software.

Nanoscale structural characterisation of the surface of the PG samples are done using a field emission scanning electron microscope (FESEM) (JEOL JSM-7600F).

The reflectivity of the PI film used (at 343 nm) is obtained by illuminating a piece of PI film with adhesive removed mounted in an integrating sphere (Labsphere integrating sphere), using

the same THG (343 nm) beam. The incident beam is first split into two by a plate beam splitter into a reference arm and a measurement arm. To reduce the fluence incident on the PI film such that carbonisation or ablation does not occur, the THG beam on the measurement arm is first defocused via a convex lens before entering the integrating sphere. A power meter, placed at one of the openings orthogonal to the PI film collects the scattered pulses diffusely reflected off the PI film, while another power meter at the reference arm provides a reference measurement to account for any fluctuations in beam fluence during measurement. Before measuring reflectivity, calibration of the integrating sphere and the power meter is first done by replacing the PI film with a diffuse reflectance standard (Labsphere Spectralon 99% diffuse reflectance standard) and measuring the average power at various fluences. These average power values are then used to normalise the measured power values at the same fluences reflected from the PI film.

The percentage transmission of PI (at 343 nm) is obtained by measuring the power of the same THG (343 nm) beam transmitted through a sample of PI film with adhesive removed. Similar to the reflectivity measurement, the incident is first split into a measurement and reference arm by a plate beam splitter, where the reference arm provides a reference power measurement. Similarly, the THG beam on the measuring arm is first defocused by a convex lens to reduce potential damage before falling on the surface of the PI film. A power meter is placed directly behind the PI film to capture all of the light that might be diffusely scattered while being transmitted through the film. Calibration of the set-up is done by measuring the average power incident on the power meter without the PI film at various fluences. As before, these average power values are then used to normalise the measured power values at the same fluences transmitted through the PI film.

A hand-held four-point probe (Suzhou Jingge Electronic Co. M-3 mini type four-probe tester) is used to obtain the average sheet resistance (R_s) across the PG formed from fsDLW. To standardise R_s measurements, 10 X 10 mm squares of PG are written. R_s is calculated with a combined square shape correction factor and a thickness correction factor of 3.51 [199]. The impact of laser and process parameters on overall electrical conductivity are investigated by writing and measuring the R_s of a 10 × 10 mm square of PG, as per the previously described methodology. Each square of PG is written with a consistent line overlap of 33% of ω_{theo} (11.6 μm).

Micro-battery (MB) preparation & characterisation

PG anodes for lithium-ion MBs are prepared directly on PI film of the same thickness as PI tape. After writing, anodes are cut out with the same laser, forming 16 mm diameter anodes. Circular copper current collectors are mechanically attached on the PG anode, forming an

effective anode area of 13 mm diameter. The anode is then assembled into a pouch cell for testing. A lithium metal cathode is used as a reference and counter. 1.3 mole of LiPF_6 dissolved in ethylene carbonate and diethylene carbonate is used as an electrolyte. Galvanostatic charge-discharge (GCD) testing and cyclic voltammetry (CV) are conducted with a battery testing system (BioLogic EC-Lab) and electrochemical workstation (BioLogic SP-300), respectively. The C-rate chosen for measurements is based on the actual galvanostatic cycling with potential limitation (GCPL) test.

4.3.2 Materials characterisation of PG

Above T_{grphtn} in the graphitisation (G) regime, PG can be formed. With an appropriate scanning strategy, arbitrarily shaped PG areas can be formed from PI.

Analysis of a representative Raman spectrum obtained from PG (**Figure 4.2(a)**) reveals a spectrum containing three distinct peaks that generally identify PG. Starting from the lower end of the spectrum, the three peaks are the D peak at 1328 cm^{-1} , the G peak at 1579 cm^{-1} (convoluted with a less distinct D' peak at 1615 cm^{-1}) and the 2D peak at 2652 cm^{-1} , all of which can be fitted with a single Lorentzian peak. The G peak arises due to vibrations (stretching) from sp^2 (flat) sites in carbon allotropes, while the D and D' peaks arise from defect-driven phonon scattering in the PG structure [200]. The presence of the 2D peak, which is the most important indicator of PG formation, originates from scattering by second-order zone-boundary phonons [201]. Additional information on the degree of disorder and defects in the graphene, the size of graphene crystallites as well as the degree of graphitisation can be obtained from the relative intensity ratios (I_D/I_G and I_G/I_{2D}) of the peaks. The relatively higher I_D/I_G ratio (1.36) of PG indicates a greater degree of disorder (and number of defects) and smaller crystallite sizes (L_a), according to the Tuinstra-Koenig relation ($I_D/I_G \propto 1/L_a$). The lower I_G/I_{2D} ratio (0.89) on the other hand indicates a relatively high degree of graphitisation. Furthermore, the PG spectra have 2D peak FWHMs approximately double than that of the G peaks, indicating that PG consists of turbostratic or disordered graphene layers (without AB stacking) [201, 202]. These results and conclusions fall in line with other reported Raman spectra of PG formation [125, 203]. The SEM image in **Figure 4.2(b)** of PG flakes nicely summarises the quantitative discussion above, showing an open porous structure of vertical and disordered graphene flakes with thicknesses of hundreds of nanometres or less. The Raman spectra of a-C in contrast, while containing a D and G peak (albeit much wider and convoluted with many smaller peaks which signal a greater degree of amorphous content [204]) does not have a 2D peak indicating extensive graphitisation. As a reference, virgin PI lacks any peaks in the same spectral region.

Figure 4.2. Chemical composition of PG. (a) Representative Raman spectra for PG, a-C and PI with important peaks labelled. (b) Representative FESEM image of PG formed with scanning. White arrows indicate pores in the 3D structure.

4.3.3 Comparison between the predicted and actual PG formation

The results of the experiments are overlaid with the temperature boundary T_{grphn} determined from the modelled temperature distribution at the top of the PI surface for predicting PG formation in **Figure 4.3**. T_{grphn} is found to be a good temperature boundary for predicting PG formation.

Figure 4.3. Experimental validation of PG formation. Comparison between T_{grphtn} , the predicted temperature for PG (dashed line) formation and identified material changes (filled squares) at the top surface of PI tape for 50 kHz, 100 kHz, 250 kHz and 500 kHz across N from 1 to 5,000 and F from 0.023 J cm^{-2} to 0.068 J cm^{-2} .

However, experimental results deviate from predictions at lower N across all f , at the top surface of PI, especially near T_{grphtn} . Where PG formation is predicted from T_{top} , only inferior a-C or ablation is found instead. This difference probably stems from the fact that ablation is not considered in the model. Because of the energy-intensive nature and constantly shifting front of ablation, the actual surface temperature would be lower than predicted [176]. However, as the temperature increases and carbonisation begins, the model becomes more accurate, as ablation is no longer expected to play any significant role in the carbonisation or graphitisation process for forming PG. Since predictions involving LLG are past ablation, therefore, this deviation does not invalidate the usefulness of the model in predicting the formation of PG.

4.3.4 Mechanisms of formation for PG

Various mechanisms and process that lead up to the formation of PG can be proposed from the results of the validation studies. Three regimes can be identified, an ablation (A) regime where only ablation is observed, a carbonisation (C) regime where carbonisation of PI is observed without the formation of PG, and a graphitisation (G) regime where carbonisation and subsequent graphitisation forms PG. These temperature regimes are defined by temperature profiles induced by the three laser parameters under investigation: repetition rate (f), fluence (F) and the number of pulses (N). Conveniently, the sequential and stepwise nature of the validation experiments allows discernment of the formation mechanisms through each regime.

PG formation begins with the accumulation of heat above the threshold fluence for ablation in the A regime (**Figure 4.4(a)**). Beginning with a single pulse at the lowest investigated fluence (0.0233 J cm^{-2}) ablation of the PI surface is observed at low f , F and N without any carbonisation or graphitisation at the top surface of the PI. Raman spectroscopy confirms the lack of carbonaceous material formed, showing none of the peaks (D, G or 2D) associated with PG (**Figure 4.3(a)**). Ablation of the PI surface is expected as the minimum fluence investigated (0.023 J cm^{-2}) falls within typically reported ranges for femtosecond laser ablation of PI [205]. At and above this threshold fluence, a combination of thermal and athermal processes leads to bond breaking and subsequent violent ejection of material from PI. As ablation is partially a thermal process, some amount of thermal energy is left over within the unablated PI and can be accumulated with subsequent pulses [176]. As f , F and N steadily increases, more heat is accumulated within the surface. f heavily influences the accumulation of thermal energy, as each individual pulse interacts with the material at timescales (fs) far shorter than that of thermal diffusion/conduction away from the local pulse interaction region (μs) in dielectrics and polymers [112, 122, 132, 186, 206]. This effect leads to f playing an outsized regulatory role compared to F or N . At low f ($< 5 \text{ kHz}$) in particular, the PI cools significantly between pulses because of the μs duration between pulses. Still within the A regime but at higher f ($> 100 \text{ kHz}$) with low F or N , no significant carbonisation takes place either because of a lack of energy or sufficient pulses for heat accumulation respectively, although some signs of UV-induced darkening in ablation craters are observed [207]. Only a minimal amount of heating can be accumulated, leading to the dominance of ablation and low predicted temperatures at T_{top} .

Figure 4.4. Mechanism of PG formation. (a) Ablation due to impinging ultrafast pulses. (b) Formation of a-C as gases and particles escape. (c) Formation of PG with graphitisation and the rapid expulsion of gases.

As f , F and N increases, the steady accumulation of heat leads to carbonisation of PI to form an inferior a-C (**Figure 4.4(b)**) beginning from 858 K in the C regime [173]. Raman

spectroscopic analysis of the irradiated spots reveal the presence of two peaks at 1331 cm^{-1} and 1582 cm^{-1} that correspond to D and G peaks, with a distinct lack of a 2D peak around 2650 cm^{-1} (**Figure 4.3(a)**). The carbonaceous material can be identified as an inferior a-C instead, similar to those formed under isothermal heating of Kapton [189]. While conductive, the a-C is not of interest in for this work because of its overall poorer electrical properties and sensing properties, which are essential for efficient electronic devices. Carbonisation marks the shift from away from ablation as discussed previously, having an outsized effect on heating, as the threshold ablation fluence for a-C is much higher than the range of F under investigation [208]. Carbonisation is driven by the increase in heat accumulation, as mechanisms for graphitisation and carbonisation of PI with UV lasers are reported to be thermally driven [209]. With increased f , the period between pulses (τ_L) reduces, and more heat is accumulated within the irradiated region with each pulse for the same N or F . The combination of photochemical and photothermal effects lead to the decomposition of imide and aliphatic groups, followed by the release of volatiles and other gases such as CO and O₂, as PI is steadily converted into a-C [170, 209]. Accumulation of these gases below the immediate surface of the PI and carbonaceous material formed also lead to an observed ballooning of the irradiated area in line with other reports [173].

Within the G regime, sharply increased localised heating with each pulse at high f ($\leq 250\text{ kHz}$) drives graphitisation of the a-C (**Figure 4.4(c)**). Graphitisation proceeds through the growth and clustering of carbon sp^2 clusters from the sp^3 matrix of the a-C, possibly through available benzene rings, leading to the formation of a distinct 2D peak in the PG Raman spectrum (**Figure 4.3(a)**) [149, 210]. Remaining oxygen and nitrogen-containing groups in PI surrounding the a-C (along with gases trapped from the formation of a-C) are forcibly and explosively removed [211]. An open, porous structure of highly disordered and defect heavy graphene flakes is formed, in contrast to the more orderly and defect-free formation of monolayer or multi-layered graphene. This open porous structure is highly conductive, with R_s measured to be as low as $40\ \Omega\ \text{sq}^{-1}$. As discussed previously, T_{grphn} is a good predictor for PG formation. Changes to PG do not stop at T_{grphn} . Increases in temperature above T_{grphn} leads to further graphitisation of PG, as measured by a decrease in the I_G/I_{2D} ratio (**Figure 4.5**). The electrical performance of PG corresponding increases as I_G/I_{2D} approaches the ideal ratio for mono-layer graphene (0.25), with the R_s of PG samples steadily decreasing to $40\ \Omega\ \text{sq}^{-1}$. The increase in temperature above T_{grphn} is driven by direct absorption of UV femtosecond pulses as graphene is highly absorptive in the UV spectrum [188]. Further increases in heat and pressure build-up from increased F causes ablative ejection of PG flakes from the PI substrate and R_s to subsequently rise again. Evidence of this phenomenon can be observed in **Figure 4.6**, where

flakes of PG are observed to be ablatively ejected away within the $10 \times 10 \text{ mm}^2$ samples, revealing the naked PI substrate below. Close-ups of the ablated PI surface reveal a pockmarked surface indicative of the explosive nature of the ejection under high pressure from the sudden release of gases during carbonisation and PG formation. Therefore, by heating the PI tape beyond T_{grphn} , graphitisation of a-C is driven to form PG. From these results, an optimised set of parameters for PG formation can be determined. PG formed at 500 kHz, 0.046 J cm^{-2} and 100 mm s^{-1} (rounded equivalent to 256 pulses).

Figure 4.5. Degree of graphitisation (I_G/I_{2D}) of PG with fluence and number of pulses. (a) I_G/I_{2D} ratios at 250 kHz within the graphitisation regime with increasing fluence and (b) no. of pulses.

Different temperatures also play a role in the morphology and arrangement of the graphene flakes in PG. At lower temperatures, the morphology of PG is distinctly more optically reflective compared to the dark, matte shade of PG at higher f , while being significantly less conductive. SEM investigation into the morphological differences between the two (**Figure 4.6**) reveals that the more reflective PG is made up of flakes that lie relatively flat and parallel to the PI substrate, as opposed to the darker PG, which is made up of porous standing flakes, as described previously. This morphological difference is possibly the result of differences in heating. At lower temperatures, less heating leads to significantly less vigorous explosive release of gases, finally results in the flattened PG structure against the open porous structure observed at higher temperatures. The lowered heating also results in less graphitisation, resulting in the lowered conductivity observed. This loss in conductivity is not preferred for MB or MSC electrodes.

Figure 4.6. Morphology of PG. (a) Field emission scanning electron microscope (FESEM) image of optically reflective PG with larger, flatter flakes. Inset: Image of reflective PG. (b) FESEM image of matte PG with standing flakes. Inset: Image of matte PG.

4.4 PG for lithium-ion micro-batteries (MB)

Optimisation of PG formation leads to a highly porous, 3D structure suitable for as an anode for 3D MBs. To demonstrate the effectiveness of PG in 3D MBs, PG anodes formed from fsDLW are assembled into coin cells for as lithium-ion half-cells for characterisation (**Figure 4.7**). Coin cells are fabricated with the optimal laser parameters of 500 kHz, 0.046 J cm^{-2} and 100 mm s^{-1} .

Figure 4.7. Fabrication and assembly of PG anode half-cell for testing. (a) Current collector ring with tabs for 3D PG anode cut out of thin ($50 \mu\text{m}$) copper sheet using fsDLW. (b) Current collector being assembled onto PG anode using tabs. (c) The backside of PG anode with folded tabs. (d) The front side of PG anode ready for assembly into the testing set-up. (e) Schematic of coin cell testing set-up with lithium metal as cathode and PG as an anode.

Charge discharge profiles of the PG anodes for the first 5 cycles are obtained at 2 C ($200 \mu\text{A}$) and subsequently for 1000 cycles at 17 C (1 mA) (**Figure 4.8(a)**). After an initial discharge capacity of $0.37 \text{ mA h cm}^{-2}$, a subsequent irreversible decrease in capacity is observed to $0.13 \text{ mA h cm}^{-2}$ at 2 C. This first cycle reduction is most likely due to solid electrolyte interphase

(SEI) formation on the PG surface and reaction of Li^+ ions with remaining oxygen-containing functional groups from unconverted PI [212, 213]. At 17 C, no large loss in capacity from the first cycle is observed, only a steady decrease from a maximum of $0.06 \text{ mA h cm}^{-2}$ to $0.03 \text{ mA h cm}^{-2}$. The available capacity even at 17 C showcases some potential for high power capacity in PG. The cyclic voltammograms obtained of the PG anodes are shown in **Figure 4.8(b)**. Measurements are taken from 0.001 to 1.5 V vs Li/Li^+ at a scan rate of 1 mV s^{-1} over 6 cycles. No appreciable loss in capacity is observed from each cycle, compared to the loss in capacity and hysteresis of CV curves typical for anodes consisting of disordered carbon structures [213]. Compared to the CV curve obtained from a reference PI sheet, PG exhibits a clear capacity to reversibly store electrochemical charge. The overall lower performance of the PG anode compared with graphite (2.5 mA h cm^{-2}) could be due to the presence of the supporting PI layer below the PG, or poor electrical contact between the copper current collector ring and the PG flakes during testing. Based on its overall capacity, PG shows potential for use in 3D MBs, but requires further optimisation and development.

Figure 4.8. Charge-discharge and cyclic voltammograms of PG anode half-cells. (a) Charge-discharge curves at 2 C and 17 C, scan rate 1 mV s^{-1} . (b) Cyclic voltammogram of PG anode and PI reference for 6 cycles. Both curves are obtained from 0.001 V to 1.5 V.

The cyclic performance of PG at different C rates is investigated next, shown in **Figure 4.9(a)**. PG is first cycled at 0.2 C for 5 cycles, followed by 2 C, 4.9 C, 15.7 C up to a maximum of 41.7 C for 5 cycles each, before 5 more cycles back at 0.2 C. Even after cycling at extremely high C rates, reversible capacity ($0.15 \text{ mA h cm}^{-2}$) is demonstrated from an initial $0.16 \text{ mA h cm}^{-2}$ during the first 5 cycles at 0.2 C. The initial performance is comparable to similar PG MBs reported without post treatment [150]. With this result, PG demonstrates the potential for high-rate reversible capacity with more optimisation. The cycling efficiency of PG over 1000 cycles is investigated next. The first cycles are discharged at 2 followed by the next 1000 at 17 C. After an initial decrease in energy capacity, the steady-state energy capacity values ($0.05 \text{ mA h cm}^{-2}$) show no appreciable drop in Coulombic efficiency even after 1000 cycles. This

impressive cyclic performance possibly results from easily accessible graphene flakes for reversible lithiation and delithiation.

Figure 4.9. Cyclic performance and efficiency of PG anode half-cells. (a) Cyclic performance and efficiency of PG at various C rates. (b) Long-term cyclic performance and efficiency of PG at 2 C. Inset: Cyclic performance and efficiency for the first 5 cycles. Left axis: Areal capacity for charging and discharging. Right axis: Coulombic efficiency.

These results show that PG can be used as anodes for lithium-ion MBs with a long cycle life up to 1000 cycles or more. Further optimisation of the PG anode can be done to improve the energy capacity to for use in smart wearables and IoT devices. One possible approach might be through the addition of doping elements [214]. The high cycling performance of PG also indicates possible strengths for applications in MSCs, which will be explored in **Chapter 5**.

4.5 Summary

In this chapter, a simple and accessible analytical formulation was developed to predict the formation of PG. Compared to other models that rely on numerical approximation, this analytical formulation was easily reproducible and useful for investigating PG formation from fsDLW. The model considered laser parameters and temperature-dependent changes to material properties to model the temperature rise and distribution across the top surface of PI. Using a temperature boundary T_{grphn} as a proxy for PG formation, different laser parameters for the

formation of PG were thus predicted. The model was experimentally validated with the fsDLW system described in **Chapter 3**, with minor deviations from predicted parameters possibly due to unaccounted ablation effects. These overall results lent more evidence to the hypotheses and observations that the PG formation was largely driven by photothermal heating, and that the formation of PG underwent an a-C regime before graphitisation to form highly conductive PG. To demonstrate the potential for PG as a 3D MB anode, lithium-ion half-cells were assembled from PG for characterisation. PG was demonstrated for use as a micro-battery anode, with an energy capacity like reported PG MBs and a high cycling capability. The work presented in this chapter is envisaged to further the development of PG devices from fsDLW and provide a useful and accessible tool to predict the formation of PG.

The tools developed and lessons learnt from this chapter will be applied to investigate the integration of PG 3D MSCs into flexible IoT devices in **Chapter 5**.

Chapter 5: Thermally localised laser graphitisation (LLG) for integrated graphene-paper micro-supercapacitors (MSCs) and electronics

In this chapter, 3D MSCs based on localised PG (LPG) are fabricated using thermally localised laser graphitisation (LLG) over thermally sensitive paper substrates as a showcase for integrated graphene-paper IoT devices. The analytical temperature model developed in Chapter 4 is utilised to identify and predict a set of laser parameters for LLG, and the LLG regime is experimentally validated with the same UV fsDLW set-up discussed in Chapters 3 and 4. The LPG formed is characterised and found to be of similar quality to previously reported PG formed outside the LLG process. LPG 3D MSCs and humidity sensors are fabricated directly on paper substrates and characterised to showcase the potential for integrated graphene-paper power sources and electronics.

5.1 Introduction

The integration of 3D power sources that can match the compact form factors of smart wearables and IoT devices is essential to effectively power such devices. Integration can be achieved with femtosecond direct laser writing (fsDLW), by forming 3D porous graphene (PG) devices directly onto new and existing devices. However, as established in **Chapter 4**, the formation of PG requires rapid heating up to extremely high temperatures above 1775 K. Heating to such high temperatures results in major difficulties in controlling the heating process to ensure that the substrate below is not damaged in the process. The challenge is therefore to develop a process that can minimise substrate damage while forming high-performance PG devices.

To meet this challenge, the analytical temperature model previously developed and detailed in **Chapter 4** can be utilised. By expanding the focus of the temperature model beyond the top surface of PI, the temperature distribution across the vertical cross-section of PI, from PI film to silicone adhesive can be modelled for different material and laser parameters. The temperatures at the top and bottom surfaces of PI rape can thus be predicted. When used in combination with temperature boundaries for graphitisation (at the top surface) and thermal damage (at the bottom), a set of parameters for a thermally localised laser graphitisation (LLG)

regime can be identified. Heating required for carbonisation and graphitisation from fsDLW is constrained at the top surface of PI such that localised PG (LPG) devices can be fabricated in-situ over thermally sensitive substrates without heating damage.

When robust precursor materials are used, the combination of both PG and substrate can offer significant advantages. For example, polyimide (PI), a popular PG precursor material is robust to thermal, chemical and mechanical stresses at low cost, alongside its wide commercial availability [125, 126, 149, 164, 169, 170, 215]. PG devices formed from converted PI combine these advantages in performance, cost and ease of fabrication. PG devices can introduce new functionality while mitigating serious disadvantages in chemical and thermal resistance in paper electronics [216]. Paper, which is made up of flexible and tough cellulose fibers, is biodegradable, recyclable and can be fabricated at low cost [217]. These advantages render paper a ubiquitous and attractive substrate for single use devices [218]. However, these strengths also prove to be a significant disadvantage. These same cellulose fibers are hygroscopic and thus highly susceptible to damage from temperature and humidity. Over the long-term, heating and liquid damage would weaken the paper structurally [219]. These disadvantages limit the fabrication of devices that require direct contact with liquids. Micro-supercapacitors (MSCs), for example, utilise gel or liquid-type electrolytes that might degrade the paper substrate [219-221]. Sensors that require direct contact with liquids, such as humidity sensors and microfluidic devices are also not suitable for the same reason [222-224]. Various physical and chemical methods have been reported to address these issues [225, 226]. Re-engineering paper or forming new paper-like materials for greater robustness and performance is one such method [227]; the printing or deposition of wax or other hydrophobic coatings such as photoresists is another [222, 228]. Unfortunately, these methods often come with significant trade-offs either in cost or re-processability [225]. To avoid these trade-offs, a simple roll-to-roll (R2R) compatible method is proposed, where commercially available PI tape is used as a thermally robust and water-resistant layer instead of re-engineering the paper substrate. PG devices are then formed in-situ through laser graphitisation of the PI layer directly above the paper substrate. Integrating conductive PG devices with paper electronics through direct laser graphitisation of attached PI tape can therefore improve the robustness of paper electronics while simultaneously improving or introducing new functionality with minimal additional complexity.

Alternatives to in-situ laser graphitisation of PI tape are inadequate. Direct attachment of ex-situ fabricated PG devices is not a suitable alternative because the overall network of graphene flakes in PG is brittle and breaks easily off the PI substrate during handling, leading to a loss in performance [149]. Direct laser graphitisation of paper to form PG is another simple alternative

to form graphene-paper electronics [140, 229, 230]. This method, however, would mechanically weaken the paper substrate as the paper substrate itself is converted into PG without adding to the robustness of the device to humidity damage. Sequential infiltration synthesis (SIS) is another alternative to protect paper-like fibrous polymer sheets from thermal damage during laser graphitisation. SIS is used to grow inorganic metal oxides on fibrous polymer sheets, which are then subsequently laser graphitised to form a layer of PG on top of the polymer sheet [231]. SIS however, requires additional material processing steps that the simple adhesion of a PI tape layer does not require. In-situ laser graphitisation of PI therefore presents the most cost effective and least complex method.

The main challenge with in-situ laser graphitisation of PI, however, is preventing damage to the paper substrate. PI tapes suitable for integration must be thin ($< 100 \mu\text{m}$) to preserve the flexibility of paper devices as well as to reduce costs. However, carbonisation and graphitisation reportedly require temperatures from 1775 K to more than 3000 K [171, 177]. With only $65 \mu\text{m}$ (tape and adhesive inclusive) separating the top and bottom surfaces of the PI tape, thermal damage to the paper substrate below PI would be unavoidable with conventional laser graphitisation. In short, precise thermal control is the key to meeting the challenge of in-situ graphitisation of PI without damage to the paper substrate.

LLG, a process developed in this chapter, solves this challenge of integrating PG devices with paper electronics. The developed analytical temperature model from **Chapter 4** is applied to predict the temperature distribution, $T(\vec{r}, t)$ across the thin cross-sectional thickness of the PI tape (**Figure 5.1(a)**) over a range of laser and material parameters. A set of laser process parameters can thus be identified for the LLG regime (**Figure 5.1(b)**). In this regime, the predicted heating induced by laser irradiation is rapidly localised at the top surface, such that a minimum temperature for graphitisation ($T_{grphn} > 1775 \text{ K}$ [177]) is reached to form LPG at the top surface while the temperature at the bottom paper substrate remains below the target temperature threshold ($T_{dmg} < 348 \text{ K}$). From the model, thermal localisation is predicted and achieved by optimising the rate of heat accumulation by UV femtosecond pulses to leverage on the high absorptivity ($> 95\%$) of PI in the UV spectrum [203]. LPG devices can thus be fabricated on much thinner ($25 \mu\text{m}$) PI films than previously reported with UV lasers alone (at a combined thickness of $65 \mu\text{m}$ with an adhesive layer), further reducing material cost and usage [203]. Beyond these optimal conditions, LPG cannot be formed due to damage to the paper substrate in the high (forming high-temperature PG (HPG) instead) and extended low-temperature regimes (HT & ELT) (**Figure 5.1(c) & (d)**) or insufficient heating in the low temperature regime (LT) (**Figure 5.1(e)**). The same femtosecond UV laser writing system from **Chapter 3** is used to experimentally verify these predictions. Thermochromic paper, which

changes colour when exposed to heat above 348 K, aids as a simple method to visualise and identify thermal damage to paper substrates. A schematic of this overall process is depicted in **Figure 5.1(f)**. Finally, the performance of LPG MSCs and humidity sensors fabricated in-situ on paper (**Figure 5.1(g) & (h)**) are tested and characterised to demonstrate the improved functionality of these graphene-paper devices. The development of low-cost, scalable, compact and sturdy graphene-paper devices from LLG is envisaged to expand the range of applications possible for paper electronics and other devices based on thermally sensitive substrates.

Figure 5.1. LLG of polyimide (PI) on paper substrates with ultrafast pulsed lasers to form LPG. (a) Schematic of predicted temperature distribution ($T(\vec{r}, t)$) in PI tape from pulse irradiation through the PI and adhesive layers. (b) Different temperature conditions relating to the formation of LPG in the localised laser graphitisation (LLG) regime, (c) PG with substrate damage in the high temperature (HT) regime, (d) no PG, LPG but with substrate damage in the extended low temperature (ELT) regime and (e) no PG, LPG or substrate damage in the low temperature (LT) regime. (f) Schematic of the femtosecond direct laser writing (fsDLW) set-up and in-situ LPG device fabrication directly on thermally sensitive paper electronics. L: femtosecond laser emitting 343 nm THG pulses at 220 fs pulse width. HWP: Half-wave plate. BD: Beam dump. GS: XY axis galvano-scanner with f-theta lens. (g) Integrated graphene-paper electronics with a LPG micro-supercapacitor (MSC) and a humidity sensor written connected with conductive silver ink. (h) LPG humidity sensor written in-situ on thermochromic (threshold 348 K) paper and subsequently removed to demonstrate a lack of damage induced by LLG.

5.2 Experimental validation of LLG for the formation of LPG

5.2.1 Materials & methods

Material preparation & experimental validation

PI tape is adhered firmly onto thermochromic paper such that LPG formation and induced thermal damage can be measured from the same sample. Femtosecond pulses are focused onto the surface of the PI tape using the developed UV fsDLW set-up (**Figure 5.1(f)**) to modify the PI at different spots, each with different fluence (F from 0.023 J cm^{-2} to 0.068 J cm^{-2}), repetition rates (f from 50 to 500 kHz), and number of pulses (N from 1 to 5,000). Raman spectroscopy is employed to study any material changes such as the formation of LPG at the irradiated spots (spot LPG).

To further verify whether the same LPG parameters can be used to form arbitrarily shaped LPG devices, these LPG spot parameters are translated into equivalent scanning parameters (as described in **Chapter 4**) to form scanned LPG. Field emission scanning electron microscopy (FESEM) is used to investigate the detailed morphology and cross-section of the LPG.

Material characterisation

Raman spectroscopy and nanoscale structural characterisation are done using Raman spectroscopy (Renishaw InVia Raman microscope) and FESEM (JEOL JSM-7600F) respectively, according to the methods set out in the previous chapter.

The chemical composition and structure of PG, LPG and PI is investigated through x-ray photoelectron microscopy. XPS spectra are obtained from scanned $10 \times 10 \text{ mm}$ PG samples using a PHI 5400 spectrometer with a 250W Al $K\alpha$ source under vacuum.

Determination of thermal damage

Thermal damage is determined by gently separating the PI tape from the thermochromic paper substrate without damaging the thermochromic coating below. While the specific formulation of thermochromic paper used would be a trade secret, the thermochromic paper generally consists of two distinct parts, a base made of conventional paper, and a thermochromic coating that reacts upon heating to form coloured regions. The thermally sensitive coating is a three-part mixture of chiefly a colour developer, colour-changing leuco dye, and a solid-phase solvent with a melting point at the temperature where colour change is required. In this case, the required temperature is 343 K. When heated above its melting point, the solvent melts, and the developer and leuco dye can react, forming a coloured compound which is preserved as the solvent resolidifies. Without sufficient heating, the leuco dye cannot undergo a chemical

reaction to its coloured form, and the coating remains uncoloured. Therefore, by attaching the PI film directly to the thermochromic coating and then subjecting the PI film to laser irradiation, whether $T_{btm} > T_{dmg}$ (second condition for LLG) can be determined by observing the presence of any colour changes to the thermochromic paper below. Any colouration (or lack thereof) of the thermochromic coating below the irradiated spots is then examined under a laser confocal microscope (Keyence VK-250 Confocal Microscope with a 50X objective.) for further analysis. The predicted and actual LLG regimes can then be compared and analysed in combination with the Raman spectroscopic results obtained. Detailed images of the thermochromic paper results are available in **Appendix C**.

To rule out the effect of photochemically-induced colouration, separate experiments are conducted with a thin glass slide between the PI and thermochromic paper, acting as a thermal barrier. Throughout the experiment no colouration is observed, therefore colouration of the thermochromic layer can be fully attributed to heating.

Micro-supercapacitor (MSC) and humidity sensor preparation & characterisation

A layer of PI is first adhered onto the paper substrate before subsequent writing via LLG to form an interdigitated in-plane LPG MSC. To reduce the resistance of current collectors, a combination of conductive silver epoxy and conductive silver ink is used to form conductive traces between the active area of the MSC and the rest of the device. The conductive silver ink and epoxy are simultaneously sintered alongside the graphitisation to form a good and secure electrical connection between the interdigitated pattern and current collector. An additional layer of PI is used to secure the joints as well as provide a “well” to contain the electrolyte.

The LPG MSCs are assembled in an argon-filled glovebox and connected to a potentiostat (VMP3, Bio-Logic Inc.) to investigate electrochemical properties. A few droplets of 1-ethyl-3-methylimidazolium tetrafluoroborate are applied on the LPG electrodes as an electrolyte and a rest time of six hours is applied to soak the electrolyte. Cyclic voltammetry (CV) and Galvanostatic charge-discharge (GCD) tests are conducted, and areal capacitances (C_A) are calculated from the CV and GCD results. The equations for the calculations are as follows:

C_A is calculated from the CV curves using through **Equation (5.1)**:

$$C_A = \frac{1}{2 \times A \times v \times (V_2 - V_1)} \int_{V_1}^{V_2} I(V) dV \quad (5.1)$$

where A is the LPG surface area and v is the scan rate. V_1 and V_2 are the potential window during the CV measurement, where $\int_{V_1}^{V_2} I(V) dV$ is the integrated area of the CV curve. C_A is calculated by the GCD curves as well through **Equation (5.2)** [125];

$$C_A = \frac{I}{A \times \left(\frac{dV}{dt}\right)} \quad (5.2)$$

where I is the discharge current, A is the LPG surface area, and dV/dt is the slope of the galvanostatic discharge curve. A simple serpentine structure is chosen for the humidity sensor to increase the available surface area and the sensor is fabricated like the MSC, with current collectors written in place before subsequent sintering/LLG. A second layer of PI is added above to secure and mask the connections such that only the LPG area is exposed to humidity.

Relative humidity (RH) sensing is achieved by applying a voltage (1 V) across the sensing area and measuring the changes in the electrical properties via a source-measure unit (SMU) (Keysight B2900A Source Measure Unit). The LPG sensor and a commercial reference temperature and humidity sensor (Sensiron SDC30) are then both placed in a lab-built environment chamber, and humidity levels are varied to investigate the response of the LPG humidity sensor relative to the reference sensor (more details included in the Methodology section). Humidity levels are reduced by purging water vapour using argon gas or increased by bubbling argon through water and channelling water vapour into the chamber. Humidity measurements are taken along with temperature, and temperature measurements are found to only vary within 1 K. The effect of temperature on LPG is therefore regarded as negligible. More details on the measurement and calculation of RH data are available in **Appendix C**.

5.2.2 Defining the LLG regime

The LLG regime can then be predicted by mapping the modelled T_{top} and T_{btm} (**Figure 5.2(a)**) with two temperature boundaries, T_{grphtn} and T_{dmg} . Based on a reported minimum temperature for thermal graphitisation previously established in **Chapter 4**, a temperature boundary of 1775 K at the top surface is chosen as the minimum temperature for the formation of LPG (T_{grphtn}) [177]. It has been reported that, for conventional isothermal heating of Kapton films, degradation occurs upon heating above approximately 850 K in ambient conditions to form a-C with a low to minimal degree of graphitisation [189]. Temperatures higher than 1775 K are required to promote thermal graphitisation, leading to the formation of LPG [177]. Effectively, the temperature can be taken as a proxy to predict the formation of LPG. Therefore, 1775 K can be taken as a useful lower temperature threshold (T_{grphtn}) to determine the formation of LPG.

Figure 5.2. Modelling and prediction of thermally localised laser graphitisation (LLG) regime. (a) Temperature distribution after irradiation of representative parameters in the localised laser graphitisation (LLG) regime. (b) Predicted temperature rise for different N and F at both the top and bottom surfaces of the PI film at 250 kHz. Two temperature boundaries are of interest. At the top surface of the PI (T_{top}), temperatures induced by pulses should be above 1775 K, an estimated temperature threshold for graphitisation (T_{grphtn}) while temperatures induced at the bottom surface (T_{btm}) should be less than 348 K (T_{dmg}) to prevent significant substrate damage. Together, both boundaries demarcate the LLG regime (shaded), where LPG is predicted to be formed without significant base substrate damage.

On the opposite (bottom) surface, the temperature diffused through the PI and adhesive layer needs to be kept below a damage threshold temperature of 348 K (T_{dmg}) for the base paper substrate. Paper has an autoignition temperature of 491 K to 519 K, but damage owing to cellulose oxidation (yellowing) can begin at far lower temperatures, starting from 353 K [232]. This cellulose damage leads to structural weakening of paper, compromising the mechanical stability of the substrate. The maximum temperature induced by the formation of LPG devices, therefore, must be below 353 K. To visualise thermal damage during experimental validation resulting from temperatures at and above 353 K, thermochromic paper, which changes colour upon heating at a similar temperature (348 K) is attached to the base of the PI film. When heating is induced by femtosecond pulses, thermal diffusion through the PI film would heat the bottom surface of the PI, causing colour changes on the thermochromic paper above a threshold of 348 K. Since colour changes due to heating in thermochromic paper are generally accurate to within 5 K, thermochromic paper can be used to visualise thermal damage to the paper above 353 K. Therefore, 348 K is an adequate temperature boundary for damage (T_{dmg}) at the bottom surface of the PI (T_{btm}).

When combined with the developed temperature model, these two temperature boundaries (1775 K at the top surface and 348 K at the bottom surface) can then be used to determine an optimal regime for LLG by defining two boundary isotherms on a plot of temperature against laser parameters. An example of the LLG regime bounded between T_{grphtn} and T_{dmg} is

visually depicted in **Figure 5.2(b)** for 250 kHz. These predicted parameters can then be compared to experimental results, which are discussed following the next section. Implementation of the modified theoretical formulation is described in detail in **Appendix C**.

5.2.3 Materials characterisation of LPG

Arbitrarily shaped areas of highly graphitised LPG are formed within an experimentally verified LLG regime. Both conditions for LPG formation are met in this regime and validated sequentially; PG is first identified at the top surface of PI tape before subsequent confirmation that no thermal damage is observed at the thermochromic paper surface.

Raman spectroscopic analysis of LPG (**Figure 5.3(a)**) reveals spectra consisting of three distinct peaks. Two of the peaks from the spot LPG spectra are the D and tell-tale 2D peaks at 1333 cm^{-1} and 2663 cm^{-1} , while the second peak is a convolution of two smaller peaks; the G peak at 1582 cm^{-1} and a less pronounced D' peak at 1616 cm^{-1} . Each of these peaks can be fitted with a single Lorentzian curve. The relative intensity ratios of the peaks are $I_D/I_G = 0.52$ and $I_G/I_{2D} = 0.84$. Raman spectra from LPG formed at lower predicted temperatures and different parameters (both spot and scanned) within the same LLG regime in comparison reveals a similar set of peaks at similar positions (with an additional D+G peak at 2984 cm^{-1}) but with a greater amount of defects and less graphitisation, based on the relative peak intensities ($I_D/I_G = 1.76$ and $I_G/I_{2D} = 1.05$) (**Figure 5.3(b)**). Out of all of the other peaks, the presence of the intense 2D peak (relative to the G peak) supports the conclusion that the material identified is PG. Furthermore, all three PG spectra have 2D peak FWHMs approximately double than that of the G peaks, indicating a similar turbostratic PG as previously observed in **Chapter 4**. These results and conclusions fall in line with other reported Raman spectra of PG formation [125, 203]. As a reference, virgin PI lacks any peaks in the same spectral region. None of the PG formed with these parameters (within the experimentally verified LLG regime) induce discolouration of the thermochromic coating below the PI layer, verifying that LPG (instead of HPG) is formed.

Further investigation of LPG under x-ray photoelectron spectroscopy (XPS) (**Figure 5.3(c)**) reveals that LPG formation leads to a drastic reduction in the atomic percentage of N and O from 21.3% to 4.7% and a corresponding increase in C from 78.7 to 95.3%. A comparison of the C1s curves of LPG and PI (Fig. 3b) reveals other changes in chemical structure from PI to LPG. Evidence of the formation of graphene can be found from the formation of a deconvoluted asymmetric sp^2 peak centred around 284.5 eV previously missing in PI and a small satellite peak at 290.5 eV that indicates the presence of $\pi - \pi^*$ transitions due to sp^2 hybridisation [233]. Conversely, other components such as C=O and the C-C sp^3 component at 285.6 eV that are

identified in PI are highly suppressed in LPG. Together, evidence from XPS supports the overall picture of carbonisation and graphitisation following the removal of N and O containing groups through the formation of LPG.

The morphological arrangement of scanned LPG is revealed under FESEM (**Figure 5.4(a)**). From the cross-sectional view, a clear layered arrangement can be observed, where the porous and networked LPG structure is localised near the surface of the PI, such that only LPG is converted from a minimally thick ($\sim 10\ \mu\text{m}$) layer of PI. This thickness includes material removed from ablation; therefore, the depth of PI converted is deeper than otherwise expected with similar reports using UV lasers [203]. Despite a greater amount of PI removal, a significant amount of PI ($5 - 7\ \mu\text{m}$) is still left unconverted to function as mechanical support for the LPG flakes, and no significant changes to the silicone adhesive layer can be observed directly. Higher magnification FESEM images of the top surface of LPG (**Figure 5.4(b)**) reveal a different angle of the highly disordered and porous network of standing LPG flakes. Together, both cross-section and top-view images support an overall picture of a material with a large 3D active surface area, important for high-performance MSCs and sensor devices.

Figure 5.3. Raman spectroscopy and x-ray photoelectron spectroscopy (XPS) of LPG. (a) Representative Raman spectra of LPG from spot irradiation in purple and PI for reference in orange. (b) Representative Raman spectra of LPG from spots (solid) with equivalent scanning parameters (dashed) in blue. (c) Representative XPS results of PI and (d) PG with respective deconvoluted peaks.

In **Figure 5.4(c)**, the same area from **Figure 5.4(a)** is imaged but at a lower magnification. At this magnification, differences between LPG and HPG formation can be deduced. All the

distinct layers from LPG to the thermochromic paper do not show any visual evidence of damage. The formation of HPG (Fig. 3g) in contrast reveals a fully carbonised PI layer as well as burnt silicone adhesive that extends down to the thermochromic paper. The top view of LPG and HPG sensors fabricated on thermochromic paper support the same depiction (**Figure 5.4(d) & (f) insets**). As deduced from the FESEM cross-section of LPG, no discolouration of the thermochromic paper is observed below the LPG sensor (**Figure 5.4(d)**), a result of insufficient heating of the solvent/leuco dye mixture within the thermochromic paper. Extensive heating evidenced from the deep colouring of the thermochromic paper is observed below the HPG sensor fabricated in the HT regime (**Figure 5.4(e)**). Heating can therefore be localised at the surface to form LPG within the LLG regime. Altogether, a picture of the LLG emerges where highly graphitised LPG is formed in-situ without thermal damage to the paper substrate for high-performance integrated graphene-paper devices.

Figure 5.4. Field emission scanning electron microscopy (FESEM) of LPG. (a) FESEM cross-section of LPG (written within the LLG regime.) Examples of pores in LPG flakes are marked out in white arrows. The dotted line represents the boundary between the unconverted PI and the silicone adhesive. The dash-dot line represents the interface between PI and LPG. (b) FESEM top view of LPG showing individual flakes and wide, porous structure. (c) FESEM cross-section of all layers after LLG including the paper substrate with thermochromic coating. The area marked by the dashed rectangle is shown in (a). (d) Image of a LPG sensor adhered on thermochromic paper, showing the lack of colouration (thermal damage) below the PI layer. (e) FESEM cross-section of all layers in after writing in the high temperature (HT) regime, scaled to (c) for comparison. (f) Image of a PG sensor (same design as (d)) also written on thermochromic paper with colouration indicating thermal damage beyond the PI layer. Inset: LPG/PG sensors before removal of PI layer from thermal paper.

5.2.4 Comparison between the predicted and actual LLG regime

The results of the experiments are overlaid with the theoretical predictions in **Figure 5.5**, where the predicted (turquoise shaded region) and actual LLG regime (purple and pink shaded regions) can be compared.

Experimental validation reveals that the no-LLG regime is correctly predicted for lower f (< 50 kHz), although the actual LLG regime for $f > 100$ kHz is larger, especially at lower F and higher N (T_{btm} lower than predicted) (**Figure 5.5**). PG and LPG formation (**Figure 5.6(a)**) is observed at 100 kHz and above. T_{top} is found to function as a simple proxy for the formation of PG in the HT (**Figure 5.6(b)**) and LLG (**Figure 5.6(c)**) regimes, while deviations between predicted and actual LLG mostly result from bottom surface predicted temperatures, T_{btm} . A distinct HT regime is also observed beyond the LLG regime where PG is formed with thermal damage induced below the PI tape. Comparatively, no LPG formation is observed at 50 kHz at all. Below 50 kHz, only ablation craters and amorphous carbons (a-C) without distinct 2D peaks are observed (**Figure 5.6(a)**) in the ELT (**Figure 5.6(d)**) and LT regimes (**Figure 5.6(e)**), similar to those formed under isothermal heating of Kapton [189].

At the bottom surface of the PI tape, T_{btm} is higher than predicted, especially when LPG is formed from large numbers of low F pulses. This anomalous result possibly arises from unaccounted interactions between high and low-intensity femtosecond pulses and the complex networked morphology of the LPG, reducing the amount of heating at the bottom surface more at lower F . This difference is not captured in the model, where material changes assume that the mechanisms of laser-material interactions do not change depending on F , f or N . More research is required to discern these differences, and future models could account for such changes to be more accurate. Unaccounted-for photochemical changes to LPG at lower F , which might have been hidden by photothermal effects at higher F , cannot be ruled out either. However, despite this difference in predictions, a clear LLG regime is still identifiable within the predicted parameters. Therefore, this deviation does not invalidate the usefulness of the model in predicting the formation of LPG.

The second notable deviation is observed between the discolouration of thermochromic paper from spot irradiation and the equivalent scanning parameters. When large areas of LPG are written with equivalent scanning parameters, only a limited set of parameters with lower N and F (and therefore a lower predicted temperature) do not induce discolouration to the thermochromic paper (**Figure 5.5**, purple shaded region) than otherwise predicted by the model. This discrepancy can be attributed to the differences in temperature profiles when comparing spot versus scanning irradiation. During spot irradiation, all incident pulses reach

the same area; therefore, changes to material properties such as thermal conductivity can be predicted by the model. During the scanning process, however, overlapping lines and pulses would lead to exposure to different effective material properties per pulse, leading to a much less uniform temperature profile than otherwise predicted. Despite these deviations, PG formed from the spot and equivalent scanning parameters (**Figure 5.3(b)**) still show similar Raman peak intensities and positions. Therefore, scanned writing parameters that fulfil conditions for LLG can still be found within the LLG regime. Other scanning strategies such as dot (raster) strategies could also help to mitigate this issue.

Figure 5.5. Comparing predicted and actual thermally localised laser graphitisation (LLG) regimes. (a) Comparison between predicted LLG regime (shaded turquoise region) and identified material changes (filled squares) at the top surface of PI tape for 50 kHz, 100 kHz, 250 kHz and 500 kHz across N from 1 to 5,000 and F from 0.023 J cm^{-2} to 0.068 J cm^{-2} . (b) Comparison between predicted LLG regime (shaded turquoise region) and colouration of the thermochromic paper (filled squares) at the bottom surface of PI tape for the same parameters. The dashed and dotted lines describe the isotherms for T_{grphn} and T_{dmg} at their respective surfaces. The purple dotted and dashed regions describe the actual range of parameters for spot and scanned LLG, respectively. (c) All four regimes (high temperature (HT), thermally localised laser graphitisation (LLG), extended low temperature (ELT) and low temperature (LT)) at the same parameters bounded by T_{grphn} and T_{dmg} .

In summary, experimental verification shows that the developed temperature model functions as a useful benchmark for identifying the LLG regime and therefore optimal parameters for the formation of LPG. Deviations from predictions include a larger experimentally demonstrated set of laser parameters for LPG formation at lower F and higher N and a smaller set of parameters for scanned versus spot LPG formation.

Figure 5.6. Carbonisation and graphitisation between the different regimes. (a) Comparison of representative Raman spectra from PG, LPG, a-C to ablated PI, normalised to the G peak. (b) Representative 50X confocal images of the carbonaceous materials formed at the high temperature (HT), (c) thermally localised laser graphitisation (LLG), (d) extended low temperature (ELT) and (e) low temperature (LT) regimes, along with the corresponding representative discolouration of thermal paper below.

5.3 LPG MSCs and electronics

5.3.1 LPG-based graphene-paper MSCs

With this deeper understanding of the conditions for LPG formation, LPG devices can then be directly fabricated and integrated onto paper substrates. An example of a paper device with an integrated LPG sensor and MSC is shown in **Figure 5.7**. The next step is then to investigate the performance of these LPG devices. Two devices, an LPG MSC and a LPG humidity sensor are fabricated and characterised individually.

Figure 5.7. LPG MSCs and humidity sensors. (a) Integrated LPG-paper electronics consisting of (b) an LPG MSC as a power source, (c) an LPG humidity sensor, silver ink conductive traces and other passive components. All LPG devices are fabricated via LLG.

A key limitation of current paper electronics is the lack of integrated site-specific energy sources that can be directly integrated onto paper electronic devices. While current collectors and MSC materials can be directly deposited onto paper substrates (with the paper acting as mechanical support), MSCs commonly require the use of a gel or liquid-type electrolyte to enable capacitance [220]. Such electrolytes however tend to be absorbed and diffused through hygroscopic cellulose when directly deposited on the paper substrate. While some paper out-of-plane MSC designs do utilise this absorption (where the paper functions as a separator in addition to acting as mechanical support), diffusion can lead to electrical shorts across in-plane MSC, or the degradation of the paper substrate below the MSC [234]. Other alternatives either rely on expensive or untested methods to treat the paper to allow for paper to resist electrolyte, or use less recyclable alternatives such as photo paper, which has a water impermeable layer added to reduce diffusion into the cellulose [219, 220, 222]. PI on the other hand is low-cost, commercially available, much more chemically resistant to most common electrolytes, and does not affect the re-processability of paper. From the FESEM images of LPG discussed previously, the unconverted PI layer below the LPG acts as a barrier, preventing the ionic liquid electrolyte from contacting the paper substrate below. Therefore, electrolyte can be directly deposited on the LPG MSC, forming a site-specific energy source that can be designed to fit the device's performance as required.

The performance of LPG MSCs directly fabricated via LLG over paper is investigated. An ionic liquid electrolyte, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄), is used to demonstrate the use of an electrolyte that would not otherwise be directly compatible with paper as well as expand the potential window and current density. The electrochemical performance of the LPG MSC is investigated by cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) measurements, and areal capacitances (C_A) are calculated based on the CV and GCD results. CV curves at scan rates ranging from 10 mV s⁻¹ to 100 V s⁻¹ are shown in **Figure 5.8(a) & (b)**. The CV profiles have rectangular shapes, showcasing the high capacitive

performance of LPG even at high scan rates of 100 V s^{-1} . This capacitive performance likely results from the large active surface area of the highly porous LPG flakes. The calculated C_A by the CV measurement is shown in **Figure 5.8(c)**. The C_A is 0.428, 0.221, 0.174, and 0.141 mF cm^{-2} at scan rate of 10, 100, 1,000, and 10,000 mV s^{-1} scan rate respectively, similar in performance to other reported PG MSCs from PI [7, 149]. GCD results are shown in **Figure 5.8(d) & (e)** at various discharge current densities from 0.1 mA cm^{-2} to 10 mA cm^{-2} . C_A based on the GCD results is also calculated (**Figure 5.8(f)**). C_A based on the GCD results (**Figure 5.8(g)**) shows similar values and trend for the discharge current density with the C_A based on the CV results. In summary, these electrochemical results demonstrate that LPG MSCs can be used as site-specific power sources for high-performance self-powered graphene-paper electronics.

Figure 5.8. Performance of LPG MSCs. (a) Cyclic voltammetry (CV) curves of LPG MCs with EMIMBF₄ electrolyte at scan rates ranging from 10 mV s^{-1} to 1000 mV s^{-1} and from (b) 2 V s^{-1} to 100 V s^{-1} . (c) Areal capacitances (C_A) calculated from the CV curves as a function of scan rates. (d) Galvanostatic charge-discharge (GCD) curves of LPG MSCs at various discharging current densities of $0.1 - 0.5 \text{ mA cm}^{-2}$ and (e) $1 - 10 \text{ mA cm}^{-2}$. (f) Calculated C_A from the GCD results versus discharge current densities.

5.3.2 LPG-based graphene-paper humidity sensors

LPG from PI also solves another key limitation of paper electronics in the measurement of relative humidity (RH). Paper is hygroscopic, and exposure to high humidity levels across long periods will cause irreversible damage. PI, in contrast, is impervious to water damage; therefore, by integrating LPG humidity sensors with paper electronics, a simple, low-cost resistive humidity sensor can be demonstrated. Humidity sensing is achieved without the need for additional hygroscopic elements.

The response of LPG to increasing humidity is first investigated. Actual humidity and temperature values are obtained from a commercial humidity sensor placed in parallel to the LPG sensor, with responses recorded every two seconds. More details are included in the Materials & methods section. The resistance across the LPG sensor is found to increase by up to 4% in a generally parabolic manner as RH is increased from 0.0% to 76.4% (**Figure 5.9(a)**). As established previously, LPG is made up primarily of smaller crystallites of graphene, as indicated by the high I_D/I_G ratio. These crystallites result in a large amount of graphene grain boundaries, which act as active water absorption sites. Water absorption from an increase in RH would then lead to a local decrease in resistivity due to reduced charge carrier transport [235]. While grain adsorption dominates for LPG, the high density of defects in LPG (intense D and D' peaks) would also result in a large role for a competing mechanism for water adsorption on graphene at edge defects. Water adsorption at edge defects results in decreased resistance instead as ionic conductive chains are formed with increasing RH [236]. The interplay of these two mechanisms most likely contributes to a large amount of variation (maximum $\sigma = 0.64$) in recorded measurements, especially at 40 to 50% RH.

The cyclic performance of the LPG sensor is measured next to investigate the repeatability of RH sensing. RH within the chamber is cycled repeatedly between maximum and minimum RH every 200 seconds, resulting in a minimum and maximum of 4.6% and 76.4% RH. The measured curves are plotted in **Figure 5.9(b)** with reference sensor data for comparison. LPG responds quickly to large and rapid increases and decreases in humidity, reaching saturation at maximum humidity. This maximum value does not reflect the maximum possible range of the sensor due to the limitations of the lab-built system. Adsorption and desorption of water molecules from LPG occur quickly enough that the same minimum can be reached with each cycle. A drawback of the current LPG sensor, unfortunately, is the undesired noisiness of the data, probably arising from the interplay of competing mechanisms discussed previously. Improvements could come about with further optimisation within the LLG regime to reduce the density of edge defects or the addition of hygroscopic materials directly onto the LPG [237]. Despite this drawback, LPG still demonstrates satisfactory performance as a humidity sensor,

with no additional complexity in fabrication. This lack of complexity enables easy integration with paper electronics. Possible future work could explore the combination of LPG humidity sensors with the previously demonstrated LPG MSCs to realise standalone graphene-paper electronics.

Figure 5.9. Performance of LPG humidity sensors. (a) Relative change in resistance versus relative humidity (RH) curve of the LPG humidity sensor. (b) Cyclic response of the LPG humidity sensor versus a commercial reference humidity sensor between 4.2% and 76.4% RH.

5.4 Summary

In this chapter, exceptional thermal control of laser induced graphitisation was demonstrated through LLG, such that LPG devices could be manufactured in-situ on paper substrates without inducing thermal damage. Temperatures over 1775 K (T_{grphn}) or more were localised at the top surface of the polyimide (PI) tape (T_{top}) to induce graphitisation. This localisation was achieved without inducing a corresponding rise in temperature above 353 K (T_{dmg}) through a combined 65 μm of PI film (25 μm) and silicone adhesive (40 μm) at the bottom surface (T_{btm}). This LLG regime was determined through a developed analytical temperature model that was used to predict the temperature distribution across the cross-section of a material due to irradiation from ultrashort pulse trains. This model took both laser and changes in material properties into account, granting the necessary flexibility for use in different scenarios. Experimental validation of the predicted LLG regime with actual LPG formation revealed a good correlation between experiments and theory.

The applicability of LPG for sturdy integrated graphene-paper electronics was then demonstrated. LPG humidity sensors and MSCs fabricated on paper were characterised. A two-pronged improvement in humidity and chemical resistance to paper electronics without re-

engineering was achieved by fabricating and integrating LPG devices in-situ. The model is also expected to be applicable to different precursor materials and substrates. For the most accurate results however, precursor materials that are well characterised thermally and optically are required. In summary, LLG is envisaged for the development of low-cost, scalable, compact and sturdy graphene-paper devices to expand the range of applications possible for paper electronics and other electronic devices based on thermally sensitive substrates.

In the next chapter, 3D material structuring using femtosecond laser interference lithography (fsLIL) will be investigated in greater detail.

Chapter 6: 3D material structuring via femtosecond laser interference lithography (fsLIL)

New form factor requirements follow the development of smart wearables and IoT devices. To ensure that 3D MBs and MSCs can be integrated into such devices, flexibility and even stretchability are essential. One approach to fabricating 3D MBs and MSCs is to directly pattern 3D structures into optically transparent substrates such as PDMS using fsLIL. In this chapter, the results of an investigation into 3D structuring of PDMS are presented. fsLIL is utilised to fabricate embedded volume phase gratings (VPGs) in PDMS. These VPGs are then demonstrated in active beam steering and tuneable spectroscopic grating applications. While the research into holographic structuring of PDMS cannot be directly applied to MB and MSC fabrication at this moment, lessons learnt from this work will be critical for future fsLIL research.

6.1 Introduction

Femtosecond laser interference lithography (fsLIL) is a powerful tool to fabricate periodic patterns directly on substrates to form high aspect ratio features. These patterns, if formed in optically transparent materials, could theoretically form large area enlargement factor (AEF) structures directly into the bulk of the material itself. Subsequent layers can then be deposited to form surface-conformal 3D MBs and MSCs [13, 30]. PDMS in particular is an attractive material for this research, with a lower fluence threshold for patterning compared to that of glass. The inherent stretchability and flexibility of PDMS is also attractive for 3D MBs and MSCs used to power smart wearables and IoT devices with conformal form-factors that cannot be achieved with rigid materials. In this research work, the developed fsLIL system is used to directly pattern 1D periodic patterns into PDMS. However, fsLIL patterning did not yield the formation of high AEF structures in PDMS that could be subsequently formed into a 3D power source. Instead, periodic patterns of altered refractive index are induced, resulting in the formation of optical 3D gratings or volume phase gratings (VPGs) throughout the PDMS substrate. These optical grating structures, as their name suggests, could be used in optical applications such as beam steering and spectroscopic applications. Even though 3D MBs and MSCs cannot be achieved using this method without significantly altering or improving the fsLIL methodology and set-up, lessons learnt from this research work will be invaluable for further development of fsLIL for the fabrication of 3D MB and MSC structures.

Manipulating the propagation of light using optical elements is the fundamental basis of research and applications in optics. Development of these optical elements follow trends and needs of researchers, and increasingly the need for flexible and stretchable (and therefore tuneable) optics has grown. This growth follows the expansion of research on beam manipulation in compact lab-on-a-chip devices, particularly in beam steering and spectroscopy [238, 239]. In this regard, the attractiveness of tuneable, flexible and optically transparent holographic devices is well established. Polydimethylsiloxane (PDMS), due to its tuneable elasticity and high transmission in the visible wavelength range can be a promising flexible transparent substrate for developing such tuneable optical elements. Various nanofabrication techniques have been developed and demonstrated to fabricate such structures on and in PDMS. These conventional processes include e-beam lithography, imprint lithography, standard UV photolithographic techniques, femtosecond direct laser writing (fsDLW), and interference patterning of photosensitive PDMS [240-245]. Diffractive components such as gratings can be fabricated with these processes, but they are mainly limited to forming surface relief or thin diffraction gratings, which are less suitable for beam steering and spectroscopic applications. These thin diffraction gratings exhibit Raman-Nath diffraction, with many unwanted diffraction orders that result in reduced diffraction efficiency (η) [246]. For increased efficiency in tuneable beam steering and spectroscopic applications, volume phase gratings (VPGs) are desired instead. VPGs can exhibit up to $\eta = 100\%$ through Bragg diffraction [246]. However, fabricating VPGs or any sort of holographic pattern directly in PDMS is much more challenging and less widely reported.

Only two methods to fabricate VPGs in PDMS have been reported so far. Using slow, focused fsDLW, VPGs are formed directly in PDMS [247]. They first allowed femtosecond filaments to form through the PDMS under a slow focusing condition, before writing across the PDMS. These filaments then induced refractive index changes along itself. In this manner, instead of a 1D line at the beam focus, a 2D “sheet” of altered refractive index was formed through the thickness of the PDMS. By drawing multiple parallel sheets with a fixed period, a VPG, instead of a diffraction grating as reported by other researchers working on fsDLW can be fabricated [243, 244]. However, femtosecond filamentation is still poorly understood and there are challenges in controlling the depth and quality of the grating. Furthermore, this method also faced the same issues as other fsDLW methods such as low resolution and higher grating width due to the diffraction limit spot size of the beam focus. Being a serial writing process, the uniformity of grating linewidth was also adversely affected by the cumulative error across a single line due to variations in fluence (F). Therefore, slow, focused fsDLW is not a good method to form high-resolution holographic patterns.

As an alternative to the fsDLW of unmodified PDMS, other researchers have varied the content of photosensitive compounds incorporated in PDMS instead, so that the existing holographic methods could be used to fabricate VPGs. Researchers tuned the photosensitivity of PDMS by varying the content of benzophenone (BPh) photoactive molecules, before using standard holographic methods to pattern volume gratings directly into the modified PDMS [248]. With an optimal percentage of BPh added, they fabricated various VPGs using both laser interference patterning and mask patterning. These VPGs were then demonstrated to tune the diffraction spectrum of an incident white light source. However, by making PDMS more photosensitive to the UV spectrum, the transparency of the modified PDMS is effectively reduced in that spectrum. This reduction in transparency has the potential limitation of reduced efficiency in beam steering and reduced spectral range for spectroscopy in the UV range. Furthermore, one of the key advantages of using unmodified PDMS is the wide availability of information on physical and chemical properties, enabling ease of use across a spectrum of applications. Modified PDMS in contrast does not have known physical and chemical characteristics readily available, which would limit the use of this technique. Lastly, the additional material processing step included also introduces complexity to the overall fabrication process. Therefore, there is a definite need for a method to directly fabricate high-resolution VPGs in unmodified PDMS for stretchable and flexible optics.

To subdue these above-mentioned drawbacks, a concept termed “ultrafast volume holography” is proposed based on femtosecond laser-assisted precise refractive index modulation (Δn) that can directly form high-resolution VPGs in unmodified PDMS. This concept follows on the insight that femtosecond repetition rate (f) can regulate heat energy accumulation in a way which is difficult to control with a long pulse laser (and impossible with a continuous wave laser) of same average power. This insight is used to precisely induce periodic Δn , forming VPGs in PDMS. Furthermore, other femtosecond pulse parameters such as the number of pulses (N), F and wavelength (λ) provide us with additional degrees of freedom, which are used to determine an optimal processing region to form VPGs with higher efficiency and minimal material damage for the proposed beam steering and spectroscopy.

6.2 Ultrafast volume holography for stretchable nanoscale structures

6.2.1 Materials & methods

Material preparation

PDMS (Dow Corning Sylgard 184®) films are prepared in a 10:1 (base to binding agent) weight ratio. The base/binding agent mixture is first thoroughly mixed in a petri dish for 1 to 2 minutes before being degassed for an hour under vacuum. The degassed mixture is then spin-coated on an acrylic plate to form thin and uniform PDMS films. Finally, the thin films are cured in an oven at 80 °C for 4 hours. After curing, the PDMS films are measured to be 180 µm thick. The cured PDMS films are then cut into approximately 15 by 15 mm squares and mounted flat onto cut-out acrylic holders. These films are secured tightly on three edges, leaving both the front and back of the sample in free space such that fabrication will not be affected by reflection or absorption of laser energy by the acrylic holder. Before exposure, PDMS films and acrylic holders are cleared of dust and organic contaminants using adhesive tape and ethanol.

Volume phase grating (VPG) fabrication

VPGs are fabricated by the interference of femtosecond pulses directly on the prepared PDMS films mounted at the plane of interference, using the fsLIL set-up developed and described in **Chapter 3**. The two collimated beams then interfere at the sample stage where PDMS films are mounted. Each beam is 0.50 mm in diameter at the interference plane with fluence (F) values within 2% of each other, measured using the knife-edge method and a translating micrometre stage. UV-Vis absorbance and transmission spectrum for PDMS can be referred to in **Appendix D**.

VPG characterisation

Angle tuning for beam steering is performed using a 532 nm diode-pumped solid-state (DPSS) CW laser (Laserglow Technologies LRS-0532), while spectrum tuning for spectroscopy is performed using a white light laser (NKT Photonics SuperK Extreme). For both the experiments, the PDMS VBGs are mounted on a stretching mount with a high precision micrometre-actuated rotation stage (angular resolution of 0.02°). For the beam steering, the Bragg diffraction direction is measured by noting the maximum power read by a power meter. For the spectroscopic applications, the Bragg diffracted spectrum at a fixed Bragg angle (13.6°) is captured by a UV-VIS spectrometer (Ocean Optics USB4000 UV-VIS Spectrometer) by a collecting lens.

Z-scan

A standard Z-scan set-up is used, with identical reference and measurement biased photodiodes connected to the same oscilloscope (Rigol MSO1104Z Digital Oscilloscope) for voltage measurements and comparison. The same THG beam used for fabrication is used for the Z-scan experiments for consistency. The THG beam is split into two via a plate beam splitter, with one directed towards the reference photodiode, and the other directed towards a plano-convex focusing lens (150 mm focal length). Unpatterned PDMS films of the same thickness (180 μm) are mounted on a sample stage that is manually scanned across 20 mm on either side of the beam focus. Two excitation conditions are investigated: 100 pulses (50 Hz) of F one order of magnitude larger compared to fabrication are captured every mm in a closed aperture scan, and 50,000,000 pulses (500 kHz) of the same F are captured almost every mm in both open and closed aperture scans, to simulate fabrication conditions.

6.2.2 Results and discussions

The developed approach is based on interfering counter-propagating 343 nm femtosecond pulses directly on the PDMS film as shown schematically in **Figure 6.1(a)**. Interference of these femtosecond laser pulses (with intensity (I_0) and phase difference (δ)) forms a grating pattern consisting of a periodic Δn following a cosine-squared distribution ($I = 4I_0 \cos^2(\delta/2)$). The details of the experimental set-up and PDMS film preparation are included in Materials & methods section. The patterned areas on the PDMS film are shown in **Figure 6.1(b)**, diffracting the visible spectrum when held against a white LED source. The PDMS film after the fabrication can directly be mounted and stretched as shown in **Figure 6.1(c)** without any further post-processing. In this way, the period of the VPG can be tuned (as shown in **Figure 6.1(a)**) for the proposed applications.

Unmodified PDMS provides high transparency, 89.6% and relatively high absorption coefficient, 1.555 cm^{-1} in the UV spectral range compared to longer λ . This property enables us to pattern the PDMS through its entire thickness when exposed to radiation of $\lambda = 343$ nm, forming VPGs instead of surface relief gratings. Gratings are characterised by investigating the diffraction regime of the gratings. Depending on λ , the periodicity (Λ) of the grating formed and the interaction length/thickness (t) of the grating, either Raman-Nath or Bragg diffraction may be exhibited. If the length of interaction satisfies the following **Equation (6.1)**, then the grating is said to be in the Bragg diffraction regime [246]:

$$t \gg \frac{\Lambda^2 n_0}{2\pi\lambda} \quad (6.1)$$

Figure 6.1. Ultrafast volume holography of VPGs. (a) Schematic of femtosecond pulses patterning of an unprocessed polydimethylsiloxane (PDMS) film placed at the interference plane. Also shown is a schematic of an embedded stretchable and flexible volume phase grating (VPG) formed and a schematic of the cosine-squared refractive index modulation (Δn) formed in PDMS. (b) Close-up of VPGs on unstretched PDMS, showing white light diffracted into blue, green and red. (c) Close-up of VPGs in manually stretched PDMS, showing white light diffracted into blue, green and red.

From the equation above, it can be inferred that the thickness of the grating should be much greater than 795 nm for diffraction to occur in the Bragg regime, considering $\lambda = 532$ nm, $n_0 = 1.415$ and $\Lambda = 1370$ nm. If the length along the optical axis of two beams of 0.50 mm diameter is considered, the length of the pulse overlap area where the interference will occur is along 2.88 mm length (at interference angle 10.0°). This value is more than an order of magnitude larger than the thickness of the PDMS films. Based on this reasoning, VPGs can be assumed to be formed via femtosecond pulse interference throughout the thickness of the film. Since the thickness of the PDMS sample ($180 \mu\text{m}$) is much greater than the required gating thickness for Bragg diffraction (795 nm), Bragg diffraction is expected to be observed from all fabricated gratings.

To validate, the theoretically calculated ($\sin \theta_B = \lambda_0/2\Lambda$) Bragg angle is compared with the experimentally measured Bragg angles for two different periodicities 1370 nm and 987 nm

(interference angles 7.2° and 10.0°). Two different lasers of $\lambda = 532$ nm and 638 nm are used and the results are tabulated in **Table 6.1**. A qualitative comparison of the fabricated VPGs diffracting white light and not is presented in **Figure 6.2**. These results conclude that VPGs can be fabricated directly into the bulk of the PDMS film and the resulting diffraction follows the Bragg diffraction formula very closely.

Table 6.1. Comparison of calculated and measured Bragg diffraction angles at 515 nm and 638 nm for sample periodicities of 1370 nm and 987 nm.

Sample period Λ	Calculated θ_B (532 nm)	Measured θ_B (532 nm)	Calculated θ_B (638 nm)	Measured θ_B (638 nm)
1370 nm ($\theta_f: 7.214^\circ$)	11.20°	12.06°	13.46°	13.98°
987 nm ($\theta_f: 10^\circ$)	15.63°	15.62°	18.86°	19.00°

Figure 6.2. VPGs in unmodified PDMS. (a) Close-up of VPG on unstretched PDMS, showing white light diffracted into blue, green and red. (b) Close-up of VPG on unstretched PDMS at a different angle without observable diffraction.

These VPGs are formed mainly due to the accumulation of thermal energy (as discussed in later sections) in PDMS which has a high thermo-optic coefficient of -4.5×10^{-4} per $^\circ\text{C}$ [249]. Since femtosecond repetition rate (f) is known to regulate thermal energy accumulation in materials, the first step to maximise Δn is to investigate the key effect of f on VPG formation [206]. Samples are fabricated for different F from 0.25×10^{-4} J cm $^{-2}$ to 1.75×10^{-4} J cm $^{-2}$ per beam and exposed from 10 s to 500 s. f from 10 kHz to 500 kHz are investigated. It is to be noted here that, enough care is taken to ensure that samples are kept free of dust, bulk impurities or surface damage, to minimise the impact of light scattering on grating formation.

To investigate the effect of f , samples are fabricated with a fixed number (50×10^6) of pulses per beam. The obtained result is shown in **Figure 6.3(a)** for $F = 3.5 \times 10^{-4}$ J cm $^{-2}$. For a range of f investigated (50 – 500 kHz), the VPGs fabricated at 500 kHz (versus 50 kHz) are found to exhibit an order of magnitude increase in diffraction efficiency (9% versus 1%) and an order of

magnitude decrease in the exposure time (100 s versus 1000 s) for the same F and number of pulses (N). A sharp increase in η above 100 kHz is observed, which indicates that high f are important in the formation of efficient VPGs. High f (500 kHz) not only increases η , but also requires less exposure time to record the pattern that can increase the fabrication speed up to an order of magnitude higher than that for the low f (50 – 100 kHz). The sharp increase in η above 100 kHz is possibly due to the transition from thermal diffusion to heat accumulation proposed in poorly conducting materials [132]. In the thermal diffusion regime, which is observed to be below 100 kHz in PDMS, thermal diffusion occurs during femtosecond pulse-material interaction before much heat can be accumulated in the material to induce refractive index changes. However, at 100 kHz and above, the decrease in the length of time between pulses allows a greater amount of heat accumulation. Therefore, a larger refractive index change is induced in the material, as observed in the increase in diffraction efficiency (to be discussed in later sections). On the other hand, too much heat accumulation at higher f is expected to degrade the performance of fabricated VPGs. Increases in refractive index are accompanied by damage induced in the PDMS along the beam path, increasing beam distortion through scattering (discussed in the next section). A good balance can therefore be found between diffraction efficiency and beam scattering. Such control over thermal accumulation is difficult with long pulse lasers (and impossible with CW lasers) because heat accumulation can already occur during the longer pulse-material interaction time at any f , possibly leading to scattering and burning damage even at low f [107].

While increased f regulates thermal energy accumulation by reducing the amount of heat that can diffuse out of the local interaction region between two consecutive pulses, thermal energy needs to be transferred to the PDMS sample via individual pulses. Therefore, increasing F and N incident on PDMS is expected to increase the amount of thermal energy transferred into the PDMS. To probe this relationship in greater detail, the effect of F and N is varied at $f = 500$ kHz. The obtained result is shown in **Figure 6.3(b)**, where four distinct regions can be identified with three corresponding thresholds defined by the borders between two adjacent regions. From the results, an optimal processing region (marked by the black dotted line) is identified, where holographic patterns are formed with comparatively high efficiency and minimal scattering damage. This optimal region covers region 2 and the lower half of region 3. Identifying this optimal processing region is important to optimise tuneable beam steering and spectroscopic performance while reducing the beam shape distortion and scattering losses.

Figure 6.3. Optimisation of VPGs with ultrafast volume holography. (a) Change in diffraction efficiency (η) with repetition rate, with fixed number of pulses (N) at $1.75 \times 10^{-4} \text{ J cm}^{-2}$. (b) Fluence (F) and N (or exposure time) thresholds for formation of VPGs, scattering damage and burn damage. The optimal processing region is marked separately with dashed lines. (c) Relationship between exposure time and F with η of VPGs.

Outside of this optimal range, three other regions can be identified as follows: Below the lowest threshold, no gratings are observed to have formed (Region 1). The lack of grating formation is experimentally verified, as there is no Bragg diffraction at the expected Bragg angles or any other angles of incidence. No other permanent changes are also observed for samples under a confocal optical microscope (Keyence VK-250 Confocal Microscope) at 50X. Between the first and second thresholds, a second region (Region 2) can be described, where VPGs are formed without any optical or scattering damage. In Region 3 between the second and third threshold, VPGs are observed along with scattering damage within the exposed area. In the upper half of region 3, the diffraction efficiency of VPGs is found to decrease beyond certain exposure time (e.g., 300 s and 100 s for $1 \times 10^{-4} \text{ J cm}^{-2}$ (green) and $1.25 \times 10^{-4} \text{ J cm}^{-2}$ (purple) as shown in **Figure 6.3(c)**). Optical or scattering damage is determined through direct microscope observation at 50X and is characterised by the formation of “tracks” induced by both beams. These tracks, which formed by unwanted changes in refractive index follow the individual beam path through the PDMS film and cross at the point where the two beams cross with each other. The magnitude of damage formation has its effect from minor refractive index changes (without any observable changes in optical transmission) to scattering losses and even to void formation (**Figure 6.4(a) & (c)**) along the tracks. These void formations happen at higher F

and exposure times where explosive ablation takes place within the PDMS bulk. Above the third threshold (Region 4), the PDMS films simply burn, catch fire and spread rapidly across the film (**Figure 6.4(b)**), if not extinguished in time. Determining this third threshold is a bit challenging, as any surface or bulk impurities in the PDMS films would cause the PDMS to catch fire before the actual threshold. However, with adequate dust and impurity control measures, this threshold can be determined for native PDMS. The above regions are to some extent analogous to the thresholds of damage formation in transparent materials proposed and observed in fused silica [116, 250].

Figure 6.4. Damage induced in VPGs. (a) Confocal microscope image (10X) of scattering damage induced by femtosecond holographic patterning. (b) Confocal microscope image (10X) of burn damage induced by femtosecond holographic patterning. All microscope images are viewed normal to the PDMS surface. (c) 20X optical microscope image of voids formed along scattering damage tracks, viewed from top-down.

To quantify the above threshold parameters, the transmittance of the grating regions are measured under normal incidence as well as their diffraction efficiencies (η) at the Bragg angle. A laser beam ($\lambda = 532$ nm) is incident on the patterned area and the transmitted power is measured by a power meter. The obtained result of normal incidence transmission measurement is shown in **Figure 6.5**. From this figure, the transmitted power is found to decrease with increasing exposure time, irrespective of F . This reduction in transmission with exposure time is due to the increased absorption and/or scattering loss of the incident beam by the grating region of the PDMS. The rate of decrease in transmission (slope of the curve) is less for lower F (0.5×10^{-4} J cm $^{-2}$ and 0.75×10^{-4} J cm $^{-2}$) compared to the higher ones (0.875×10^{-4} J cm $^{-2}$

and $1.0 \times 10^{-4} \text{ J cm}^{-2}$). This is because at low F there are lesser number of photons available to break the chemical bonds and to form monomers that could have caused scattering loss. This trend can also be observed from **Figure 6.3(b)** where (in Region 1) only minor scattering is expected for $0.5 \times 10^{-4} \text{ J cm}^{-2}$ and $0.75 \times 10^{-4} \text{ J cm}^{-2}$ even towards 500 s exposure time. With higher F , more thermal energy can be accumulated even at very low exposure time to start breaking the polymeric backbone of PDMS, causing much larger refractive index changes (Region 2) and scattering losses due to damage (Region 3) throughout the exposed area. This damage leads to a drastic loss in transmission, starting from 200 s for $0.875 \times 10^{-4} \text{ J cm}^{-2}$ (green dashed line) and even earlier (100 s) for $1.0 \times 10^{-4} \text{ J cm}^{-2}$ (purple dotted line). With continued accumulation of photothermal energy with exposure time, the PDMS films then start to burn and char, as observed in Region 4 in **Figure 6.3(b)**.

Figure 6.5. Relationship between transmitted power, and F and exposure time. Transmitted power is measured using a separate characterisation set-up.

A deeper analysis is necessary to understand the formation mechanism of Δn (that lead to the formation of the VPGs) and the observed damage features in the optimal processing region described above. Unlike conventional femtosecond interactions, the observed refractive index changes in PDMS are expected to mostly due to linear single-photon absorption and heat accumulation from high f patterning [251, 252]. A series of Z-scan experiments are conducted to investigate potential mechanisms for pulse-material energy transfer (Materials & methods). Low f experiments are done to investigate purely electronic nonlinear effects due to F (at fabrication conditions), while high f experiments are done to investigate the combination of electronic and thermal nonlinearities (from the accumulation of thermal energy at high f), at conditions close to the fabrication parameters used.

The closed aperture Z-scan at low f (**Figure 6.6(a)**) shows no significant changes in transmitted intensity across the focal area, indicating a lack of significant electronic

nonlinearities. This result is as expected because no significant electronic nonlinear effects are involved in the absorption of pulse energy (in the range of 10^8 W cm^{-2}) [107]. Since no significant effects are observed in the closed aperture scan, an open aperture scan is not conducted.

In the closed aperture Z-scan at high f (**Figure 6.6(b)**), a significant change in the transmission is observed, with a rising edge and a peak, followed by a shorter peak as the sample is scanned towards the detector to the right. Since the result of this scan is inconclusive, an open aperture Z-scan is conducted using the same parameters to investigate the effect of nonlinear absorption. A second curve is obtained in **Figure 6.6(b)**, which indicates some measure of saturable absorption (peak) offset from the centre. An adjusted Z-scan curve (closed divided by open aperture) (**Figure 6.6(c)**) then reveals an asymmetric curve, offset from the centre. This result indicates that there is a nonlinear change in refractive index due to thermal effects (i.e. thermal lensing) where n_2 is negative. It is to be noted that the sample undergoes a permanent refractive index change during high f irradiation, and this is the main cause for the shift and asymmetry in the Z-scan curves. Therefore, the conclusion is that thermal accumulation from high f is the main mechanism of refractive index change and damage formation in PDMS. This result is expected as the pulse intensities (maximum 0.8 GW cm^{-2}) in use are far below the expected terawatts (or higher) range to induce any significant nonlinear interaction [107]. Therefore, the nonlinear effect of the highly intense pulse is expected to give negligible contribution (although cannot be ruled out completely) to the refractive index change of PDMS.

While the photon energy from the laser is selectively absorbed only by the Si-C bonds, heat accumulation is required to break the stronger Si-O backbone. PDMS is mostly transparent (89.6%) to UV wavelengths. Thus, only up to 10% of the photons (not considering reflectance) can interact with the PDMS. These photons are absorbed by the polymeric chains that make up PDMS, comprising of a repeating Si-O backbone with two pendant methyl groups bonded to the Si atom. Energy absorption by the chemical bonds leads to chemical changes in PDMS due to photochemical and/or photothermal mechanisms [251]. In the photochemical process, chemical bonds break when the incident photon energy is higher than the binding energy of that covalent bond [252]. In PDMS, the binding energies of Si-C, Si-O and C-H bonds are 3.3 eV, 4.7 eV, 4.3 eV, respectively [252]. Since the incident photon energy of the laser (343 nm) is 3.6 eV, only the Si-C bonds can directly absorb these photons and liberate the methyl groups from the Si-O backbone via the photochemical process. From **Figure 6.3(b)**, a threshold for photochemical changes alone is observed to be at $F = 0.25 \times 10^{-4} \text{ J cm}^{-2}$, where only grating formation without scattering damage is observed in fabricated VPGs. On the other hand, the other two bonds having higher binding energies cannot absorb these photons. Breaking the Si-

O backbone, which would cause the breakdown of the entire polymer into smaller chains, would require energy from the accumulation of heat energy instead. These bonds are broken via a photothermal mechanism, where the heat energy absorbed by PDMS from pulse-material interaction accumulates and overcomes the covalent binding energy [252]. When bonds are broken, monomers or radicals such as crystalline Si (c-Si) could be formed [252]. As a result, the refractive index of PDMS changes and there is damage formation or ablation (**Figure 6.7**) in the sample.

Figure 6.6. Z-scan at high and low f . (a) Normalised signal from Z-scan done at 50 kHz, using the 343 nm femtosecond laser used for VPG fabrication. The averaged signal from 100 pulses is taken at each position. (b) Normalised closed and open aperture signals from Z-scan done at 500 kHz, using the 343 nm femtosecond laser used for VPG fabrication. (c) Normalised and adjusted aperture signals from Z-scan done at 500 kHz, using the 343 nm femtosecond laser used for VPG fabrication. The averaged signal from 500,000 pulses is taken at each position.

Figure 6.7. Surface ablation (black arrow indicate examples) observed on the surface of patterned PDMS. Surface ablation is centred above the patterned area.

More heat energy can be accumulated by either increasing the F , f or N to start breaking the polymeric backbone of PDMS. As a result, refractive index modulation and other induced features (scattering damage, burning) increase as heat is accumulated in the local interaction region. The interference of two beams creates a cosine-squared spatial intensity distribution ($I = 4I_0 \cos^2(\delta/2)$) with maximum intensity at the crest and vice versa. Following this intensity distribution, a maximum change in the refractive index (Δn) will occur at the maxima region (crest) and the change gradually decreases towards the minima (trough) of the pattern. A schematic representation of such a refractive index modulation in the VPG is as shown in **Figure 6.8**. Refractive index change results from the breakage of chemical bonds and formation monomers as described in the previous section. Δn is proportional to the number of monomers formed (maximum being at the crest), which in turn depends on F , the exposure time (or N) and f . When F of both beams increase equally (with all other parameters are unchanged), the amplitude of the cosine-square variation increases only in the areas of constructive interference (crests) as shown in **Figure 6.8(b)** in the manuscript. Thus Δn will be maximum at the crest region and minimum at the trough. The refractive index modulation will increase with increasing F . On the other hand, when N of each beam increases (F being fixed), the amplitude of the intensity at crest does not increase as shown in **Figure 6.8(a)**. However, a greater number of photons interact with PDMS with time and results in an increase in Δn at the crest relative to the trough region. Thus, the increase in both F and N increases the refractive index modulation of the grating. Δn is calculated using **Equation (6.2)** [253]:

$$\eta = \left[\sin \frac{\pi d \Delta n}{\lambda \cos \theta_B} \right]^2 \quad (6.2)$$

Based on the obtained results, for $F = 3.5 \times 10^{-4} \text{ J cm}^{-2}$ (100 s, 500 kHz), Δn of 1.95×10^{-4} . Therefore, refractive index changes in PDMS are due to incubation or the accumulation of both photochemical and photothermal effects in both the high and low-intensity regions of the

interference pattern. Furthermore, depending on the required application, efficiency can be optimised with minor scattering loss and beam distortion by choosing proper parameters.

Figure 6.8. Proposed mechanisms of VPG formation with ultrafast volume holography. (a) Effect of number of pulses (N) (or exposure time) on Δn and width of n_{max} , where $x < y < z$. Refractive index saturated from y no. of pulses onwards. (b) Effect of pulse F on Δn and width of n_{max} where $I_1 < I_2 < I_3$. Refractive index saturated from I_2 onwards.

The change in Δn is reflected in the efficiency (η) curve shown in **Figure 6.3(c)**, which shows that the efficiency continuously increases with time (N) for $0.5 \times 10^{-4} \text{ J cm}^{-2}$ (blue solid line) and $0.75 \times 10^{-4} \text{ J cm}^{-2}$ (red dashed line), with a higher rate for $F = 0.75 \times 10^{-4} \text{ J cm}^{-2}$. This observed increase in η is due to the increase in Δn due to the differential rates of bond breaking at the crest and trough regions of the exposed area as discussed above. However, gratings fabricated at $1.0 \times 10^{-4} \text{ J cm}^{-2}$ (green dotted line) and $1.25 \times 10^{-4} \text{ J cm}^{-2}$ (purple dotted line) reach a maximum η of 6.81% and 7.41% at 300 s and 100 s respectively before dropping rapidly. Furthermore, since power is normalised for both 0th and 1st order diffraction efficiency calculations, this decrease in efficiency cannot be due to scattering losses and/or beam distortion by the damages in the sample. This observed maximum attainable η for $1.0 \times 10^{-4} \text{ J cm}^{-2}$ and $1.25 \times 10^{-4} \text{ J cm}^{-2}$ is postulated to be due to the interplay of two convoluted phenomena: the decrease in Δn and the increase in the width of the area of greater refractive index (crest region) after certain F and N . After a certain point (at maximum η), the refractive index at the crest is expected to reach a saturation value while still increasing at the trough regions. Therefore, Δn between crest and trough rather decrease afterwards. Secondly, it is hypothesised that the width of the areas of greater refractive index increase due to the increase in N or F . As refractive index change is saturated, it results in a gradual expansion of the areas of changed refractive index relative to the original PDMS (**Figure 6.8(a) & (b)**) leading to the refractive index distribution to deviate from the original cosine-squared distribution. Thus, regardless of F , the width of the crest area is expected to increase with increasing exposure time, as more

bonds are broken in the crest regions (which are above the threshold F for bond breaking). This effect is analogous to the duty cycle in binary gratings where efficiency gradually increases with duty cycle until a maximum value at 50% duty cycle before decreasing [254]. Similarly, an increase in width would be expected to result in an analogous rise and fall of efficiency for the VPGs.

To gather some insights on the effects of both these phenomena, FDTD simulations are performed by modelling the described Δn [255]. It is not straight forward to mimic exactly such kind of refractive index modulation that would have formed when saturation takes place at the crest region. However, a simulation model that could represent approximately such kind of refractive index modulation could be attempted. Two material blocks are generated with cosine square variation of refractive index having a minimum refractive index of 1.45 (for native PDMS) and maximum refractive index equal to $1.45 + \Delta n$ as shown in **Figure 6.9(a)**. Here the cosine square refractive index modulation is represented by the gradient of colour where deeper colour represents maximum refractive index value and vice versa. The thickness of these two blocks are denoted as t_L and t_R for the left and right block respectively. This cosine square refractive index modulation is generated by writing a script and then imported as an object for the simulation. Then another block of uniform refractive index $1.45 + \Delta n$ and width w is created and inserted in between the first two blocks as shown in **Figure 6.9(b)**. The uniform colour of the block in the figure represents a constant refractive index throughout the whole block. These three blocks together form a unit cell of width $t_L + t_R + w$ that is equal to the period (Λ) of the VPG. Here period $\Lambda = 1370$ nm as per the fabricated sample. In the next step, this unit cell periodically is repeated with a lattice constant of 1370 nm as shown in **Figure 6.9(c)**. Parameter dc is defined in **Equation (6.3)**, where

$$dc = \frac{w}{t_L + w + t_R} \quad (6.3)$$

dc is varied by changing the width (a) of the middle block with respect to the period of the grating. Using this model of VPG, Bragg diffraction is analysed for a monochromatic plane wave source at an angle of incidence equal to the Bragg angle 11.19° . The variation of efficiency (η) with dc as obtained from the simulation is provided in **Figure 6.9(d)**. As can be seen from the figure, the efficiency (η) increases with dc from 0.3 towards 0.5 – 0.6 and then decreases afterwards. Although this is not the exact representation of the actual refractive index modulation, an approximate validation for the decrease in efficiency as per the experimental observation is still observed. The 0th order and the Bragg diffracted peaks for each dc , (obtained from the simulated far field diffraction) is also shown in **Figure 6.9(e)**. It shows that the efficiency of the Bragg diffracted spot is maximum for $dc = 0.5$ and less for other values. It

should be noted here that, in simulation a finite number of such unit cells are taken to form the VPG and used perfectly matched layer (PML) boundary conditions for the calculation of far-field diffraction pattern. Thus, the accuracy of the result is limited by the memory requirements of the computer.

The next part of the simulation is to study the sole effect of refractive index modulation on the diffraction efficiency. For this purpose, the cosine square intensity distribution is kept, and the refractive index modulation (Δn) is altered between the maximum (crest) and minimum (trough) point in the range from 1.0×10^{-4} to 9.0×10^{-4} . The obtained simulation result is shown in **Figure 6.9(f)**. As can be seen from the figure, η decreases as Δn decreases from 9.0×10^{-4} to 1.0×10^{-4} . Thus, the reason for the decrease in η beyond certain N , can be the convolution of two effects as postulated in the manuscript, is validated by the simulation results.

Further work needs to be done to independently verify the relative contributions of the variation of both the Δn and duty cycle with time. The existence or relative contributions either cannot be determined, as neither the variation of Δn nor the variation of the duty cycle analogue (dc) with time can be independently verified in the experiments. One possible method to tackle this hypothesis would be to use a high-resolution differential interference contrast (DIC) method for future investigations [256, 257].

Figure 6.9. FDTD simulation elements and results. (a) Imported objects with cosine square refractive index variation where the colour gradient represents such refractive index variation with deeper colour indicating higher refractive index and vice versa. (b) Unit cell with a uniform block of refractive index $1.45 + \Delta n$ sandwiched between the left and right block. (c) VPG formed by periodic repetition of the unit cell having a period $t_L + t_R + w$. (d) Variation of efficiency (η) with dc . (e) Far field diffraction pattern for varying dc . (f) Variation of efficiency (η) with Δn .

Lastly, to validate the fabrication process, the fabricated VPGs are demonstrated in two different applications, in beam steering and spectroscopy. Beam steering devices are important

to quickly and accurately change the beam path for applications in laser communications, laser detection and ranging, and there is a need for compact beam steering devices, of which tuneable Bragg-type gratings are the most heavily researched [258-260]. To demonstrate the use of a PDMS VPG as a tuneable beam steering device, a VPG with a period of 987 nm is mounted on to a mechanically actuated stretcher set on a high precision rotation stage. The same 532 nm laser as used previously is used for this demonstration. The incident beam is fixed in position, and the stage is manually rotated and shifted to keep the beam incident directly on the grating, as the sample is stretched in different steps (**Figure 6.10(a)**). Bragg angle values are taken from 0% to 20% strain at 5% intervals, and a graph of Bragg angle versus strain is obtained (**Figure 6.10(b)**). Losses in η are not considered for this short demonstration. From the results, there is a good fit between the obtained Bragg angle results (red dots), and the theoretical Bragg results (red dotted line), with a maximum error of 3.23% at 10% strain. The observed error is expected, due to some slipping of the PDMS out of the stretching mechanism, resulting in a consistently larger Bragg angle than otherwise expected. Other sources of error also include deviation from expected non-uniform stretching over the grating, as other researchers have observed [261]. Therefore, by simple rotation and mechanical stretching, a relatively precise Bragg angle change of 2.42° over 20% strain is achieved for beam steering applications.

Secondly, a tuneable transmission-based spectroscopic grating, using a fabricated VPG is demonstrated (**Figure 6.10(c)**). A collimated beam from a supercontinuum laser (NKT Photonics SuperK Extreme) is incident on VPG of a period of 987 nm and manually stretched at the fixed Bragg angle of 13.60° . The diffracted spectrum is collected via a fibre coupler into the spectrometer (Ocean Optics USB4000 UV-VIS Spectrometer). To investigate the changes in the diffracted spectrum, spectrometer readings are taken at different strain percentages from 0% to 9%, and the results are plotted in **Figure 6.10(d)**. Each spectrum measurement is normalised with respect to the peak spectrum data of that measurement for ease in comparison and compensating losses due to decrease in thickness or additional scattering from non-uniform stretching [248]. Across 0% to 9% strain, the peak λ linearly shifts from 644 nm to 770 nm, while the FWHM of the peak gradually increases. The spectrum also indicates that there is minimal out-of-band transmission at each Bragg angle with minimal side-lobes. Visually, a similar spectrum change (at a different Bragg angle) is captured by the shift from a peak in the green range to the red range (**Figure 6.10(e)**). While not optimal, the fabricated VPGs could be potentially used as a tuneable transmission-based spectroscopic grating.

Figure 6.10. Tuneable beam steering and spectroscopy demonstrated with stretchable and flexible VPGs in PDMS. (a) Schematic of VPG as a free space beam steering device via rotation and stretching for a single λ (532 nm). (b) Change in Bragg angle in relation to strain (%). Dotted line indicates the expected Bragg angle, while the plotted points indicate the measured angles. (c) Schematic of VPG as free space transmission-based spectroscopic grating with a white light source. (d) Change in peak λ and spectral dispersion in relation to strain (%). (e) Demonstration of the tuneable spectroscopic transmission grating using a supercontinuum (SC) laser. (i) 0th order and 1st Bragg order diffracted beam. (ii) & (iii) Close-up of the diffracted spot before and after stretching, marked in white.

6.3 Summary

In conclusion, a novel concept of fabricating tuneable and flexible VPGs for active beam steering units and tuneable spectroscopic optical elements is demonstrated. A single step ultrafast volume holographic patterning process directly patterns VPGs into unmodified PDMS. Using this process, a VPG with Δn of 1.95×10^{-4} in unmodified PDMS with less than $1 \mu\text{m}$

periodicity. Further work can be done to independently verify the relative contributions of the variation of both the Δn and duty cycle with time. It is to be mentioned that these demonstrated applications in free space could well be extended to PDMS based flexible and compact lab-on-a-chip systems with the addition of more reliable and compact non-mechanical stretching systems to control PDMS tuning. Other potential applications such as in hybrid optics can be envisioned by conformally laying the fabricated VPGs over rigid optical components such as lenses. Furthermore, by using multiple pulse trains at different angles simultaneously with additional provisions for sample scanning, this method opens the door for facile fabrication of large-area tuneable 2D and 3D photonic crystals and metamaterials. This demonstrated single-step method will be useful to a larger audience seeking efficient techniques for integrating complex periodic patterns into compact lab-on-a-chip photonic systems.

Even though the original goal of forming high AEF structures in PDMS was not met, the formation of VPGs across the bulk of the PDMS showcases the overall validity of the original concept. Research presented in this chapter will therefore be critical to guide future research into direct patterning of substrates for 3D MBs and MSCs. For example, like how η increased then subsequently decreased with number of pulses and repetition rate, the depth of patterns formed in other optically transparent materials would be expected to follow similar trends. Even though the mechanisms of laser-material interaction are different, the same principles apply. As pulse energy within “troughs” of the interference pattern surpasses the threshold for material ablation, for example, areas within the troughs of the interference pattern will get unavoidably ablated away as well, resulting in a maximum aspect ratio formed within the bulk of the material. A focus on improving the contrast and fluence of fsLIL patterning is therefore required to fabricate the targeted high AEF structures in future research.

The next chapter concludes and summarises all the research presented in this thesis, and suggestions for future research are discussed.

Chapter 7: Conclusion and recommendations for future work

The overall conclusion of the thesis is presented in this chapter, along with the major contributions of this research work. The chapter ends with several recommendations for future research directions.

7.1 Conclusions

Today's 2D MBs and MSCs are unable to meet the needs for the next generation of smart wearables and IoT devices, limited in energy capacity to power the more rigorous requirements for processing, communication, and sensing. To circumvent this limitation, researchers have been looking to exploit the third dimension to form 3D MBs and MSCs that have large surface areas, forming power sources with high-performance in the same footprint. However, a major challenge is that conventional strategies for fabricating 3D MB and MSC structures, such as using micro-machined silicon, templates, template-less growth, or in-situ deposition are costly and complex. Meeting this challenge requires the development of alternative methodologies that are cost-effective and scalable such as femtosecond direct laser writing (fsDLW) and femtosecond laser interference lithography (fsLIL).

To ensure the reliability of both fsDLW and fsLIL, a set-up and method was first developed to monitor in-line several key laser parameters from the multi-wavelength femtosecond laser used: namely repetition rate (f), number of pulses (N) and fluence (F). Monitoring of these laser parameters during fabrication of 3D structures greatly improved process reliability by ensuring that unwanted variations in laser patterning parameters were caught and removed.

Further improvements in process reliability were developed specifically for the fabrication of 3D porous graphene (PG) structures using fsDLW. An overall methodology beginning from the design of PG devices to the characterisation of PG devices was investigated and demonstrated, using a lab-developed fsDLW system consisting of a femtosecond laser with the in-line monitoring system developed previously, and a galvano-scanner fitted with a f-theta lens. The first step of the overall methodology was to add additional design elements called "wings" to PG device designs. Addition of these wings was a simple method to allow for complete acceleration and deceleration of the galvano-scanner mirrors during patterning. In doing so, uneven fluence distribution across the critical sections of designs were minimised. In the next step, after the design is then converted into processes parameters by the laser control

software, a method to secure polyimide (PI) films and tape was developed. Polydimethylsiloxane (PDMS) films were utilised for their high adhesive friction to secure the underside of PI films and tape so that uneven heating inherent to the fsDLW process did not cause curling and warping of the PI samples. This method ensured that the PI samples are not exposed to uneven fluence during patterning. Next, a method to ensure consistent positioning of PI samples in the z-direction was developed. The distance from the surface of the optical table to the focal point of the galvano-scanner's f-theta lens was first determined using focused pulses and thermal paper. A height gauge was then used to reliably and repeatably set the z-height of the sample stage. The last step in the overall methodology was the characterisation of PG samples with a combination of Raman spectroscopy, field emission scanning electron microscopy (FESEM), x-ray photoelectron spectroscopy (XPS) and laser confocal microscopy to investigate the morphology and chemical composition of PG formed. In summary, this methodology enabled the reliable and repeatable formation of PG for 3D power sources, which was then utilised in subsequent research into PG formation and integration into smart wearables and IoT devices.

As a complementary alternative to fsDLW, a two-beam fsLIL set-up capable of direct patterning of substrate materials was also developed. The low temporal coherence of femtosecond pulses and high fluence required for patterning imposed special considerations that had to be accounted for all parts of the interference set-up, namely beam splitting, angle control and optical path calibration. Splitting of femtosecond pulses to maintain temporal coherence was achieved by using a plate beam-splitter with a plate compensator. Illumination angle control was achieved with the development of a six-mirror system to reduce the incident angle of pulses for low angle interference (i.e. large pitch patterning). This system allowed the creation of 3D structures with enough space for subsequent MB and MSC layer deposition. Lastly, a simple method for optical path calibration was developed to ensure that the optical path difference (OPD) can be kept within the coherence length for interference patterning. Interfering beams were recombined at the interference patterning plane and the interference pattern of the recombined beam is projected onto a far wall. These pitch, distortion and tilt of these fringes was then used to calibrate the OPD for interference patterning at the original interference plane. These same considerations were also used to develop a four-beam umbrella interference setup for future research and investigations into more complex periodic patterns.

To guide parametric studies on the formation of PG from fsDLW, a simple and accessible analytical formulation was developed to predict PG formation through a temperature distribution. This model took into consideration both laser and temperature-dependent material parameters to model the temperature rise in PI due to fsDLW. By combining this model with a

reported temperature boundary ($T_{grphn} = 1775$ K) for graphitisation, laser parameters required for PG formation were predicted using temperature as a proxy. These predictions were experimentally validated through the fsDLW system and methodology developed previously. Only minor deviations from these predictions were observed, mainly due to ablation effects that were originally not considered. The experimental and theoretical predictions together lent further evidence of the hypothesis and observations from other researchers that PG formation was largely driven by photothermal heating, and that amorphous carbon (a-C) was formed as a transitional material during PG formation. To demonstrate the usefulness of PG in 3D MBs, 3D MB lithium-ion anode half-cells were assembled and characterised. The demonstrated energy capacity was comparable to similar PG MBs, and the high cycling capability showcases the potential for further development and optimisation of PG for 3D MBs. Further development of PG devices is envisaged with this conclusion of this work, as the model developed will be useful for predicting and understanding the formation of PG from fsDLW.

Research into the integration of PG power sources into smart wearables and IoT devices was investigated next. This same analytical temperature model was adapted to achieve exceptional thermal control during the formation of PG. Heating to drive carbonisation and graphitisation process was constrained only at the top surface of PI, keeping the underlying substrate below the PI undamaged by excessive heating. This process was termed thermally localised laser graphitisation (LLG), forming localised PG (LPG). By considering the modelled temperature distribution across the cross-section of PI tape, the temperature rise induced by laser irradiation at the top and the bottom of the PI tape was predicted. Two temperature boundaries, graphitisation temperature at the top surface (T_{grphn}) and a temperature threshold for substrate damage (T_{dmg}) at the bottom surface was used in combination with the temperature distribution to predict a LLG parameter regime, where $T_{grphn} > 1775$ K, and $T_{dmg} > 348$ K. These predictions were experimentally validated through the same fsDLW system, and the predictions were shown to correlate with experimental results. Integration of these PG devices using LLG was demonstrated with the fabrication and characterisation of LPG MSCs and humidity sensors directly on paper. The further development of low-cost, scalable, compact and sturdy graphene-paper devices is envisaged to expand the range of applications possible for LPG devices on other thermally sensitive substrates.

fsLIL for direct periodic patterning of optically transparent materials was investigated using the fsLIL set-up developed. While the original intention of patterning 3D structures in PDMS for 3D MBs was not achieved, the structures formed were used as volume phase gratings (VPGs) in optical applications instead. These VPGs were patterned directly in unmodified PDMS, where reflective index modulation (Δn of 1.95×10^{-4}) was achieved through the process termed

ultrafast volume holographic patterning. These same VPGs were characterised for active beam steering and tuneable spectroscopic applications, where the VPGs were shown to change the direction of the diffracted beam and change the spectral range required with mechanical stretching of the VPGs. The outcome of this work was expected to enable further development of 2D and 3D photonic structures on lab-on-a-chip systems, as well as drive future research into direct periodic patterning of substrates for 3D MBs and MSCs.

In summary, the research work presented in this thesis showcased the development of fsDLW and fsLIL for fabricating 3D power sources in a scalable and cost-effective manner. It is envisaged that this research will drive further development of integrated 3D MBs and MSCs for smart wearables and IoT devices.

7.2 Major contributions

The major contributions of this research are summarised as follows:

1. An in-line monitoring set-up and methodology is developed to monitor fluence, repetition rate and the number of pulses during fabrication to ensure that unwanted deviations during laser patterning can be spotted and excluded.
 - a. This set-up incorporates optical components and measuring equipment to reliably monitor these three laser parameters down to the emission of a single femtosecond pulse.
2. A fsDLW methodology to ensure the uniform formation of PG from fsDLW by minimising uneven exposure of fluence during patterning.
 - a. This methodology includes the use of PDMS films as a temporary adhesive layer to secure PDMS, the addition of wings to PG device designs, and a method to determine the focal height from the optical table surface, an easily accessible reference datum. This method improves the uniformity of PG devices as illustrated and improves the repeatability of material properties across different designs and geometries.
3. A fsLIL two-beam and four-beam set-up for direct patterning at high fluence and large pitches.
 - a. This set-up takes into consideration the need for patterning at high fluence as well as the low temporal coherence of femtosecond pulses. Optical components for beam splitting and angle control are also chosen such that low angle ($< 10^\circ$) large pitch ($> 1 \mu\text{m}$) periodic patterning is achievable.
 - b. A methodology to quickly calibrate the fsLIL set-up is also developed to ensure that the overall OPD between the different arms are kept within the coherence

length of the femtosecond pulses.

4. An analytical temperature model is developed to predict the formation of PG via temperature rise for 3D MB and MSC applications.
 - a. By taking into consideration laser and temperature-dependent material properties, the temperature rise at the surface of PI tape can be determined. Combined with a temperature boundary for graphitisation of PI ($T_{grphn} > 1775$ K), laser parameters required for the formation of PG can be predicted.
 - b. This temperature model is experimentally validated with a fsDLW set-up across a range of fluence from 0.023 to 0.068 J cm⁻², from 1 to 5000 pulses, and from 50 kHz to 500 kHz. PG formation is found to occur with parameters that are modelled to raise surface temperatures above 1775 K, correlating well with experimental predictions. Possible PG formation mechanisms in three distinct regimes, ablation, carbonisation and graphitisation are discussed in detail from the parametric study done.
 - c. The surface morphology, chemical composition and electrical properties of PG are characterised with Raman spectroscopy, FESEM, electrical four-probe testing and laser confocal microscopy. The PG characterised is found to correlate well with other reported works on PG. The PG formed is highly conductive, with a minimum R_s of 40 Ω sq⁻¹.
 - d. The PG predicted is demonstrated for MB applications. Optimised PG anodes are fabricated and assembled into lithium-ion half-cells for characterisation and testing. Through cyclic voltammetry and charge-discharge cyclic testing, PG anodes are found to have a energy capacity of 0.15 mA h cm⁻² at 0.2 C, with an energy capacity of 0.030 mA h cm⁻² maintained over 1000 cycles at close to 100% efficiency at 17 C. The performance of the demonstrated PG MB is comparable to similar MBs, and the high cycling capability showcases the potential for further development and optimisation of PG for 3D MBs.
5. The same analytical temperature model is used to predict laser parameters for LLG for the integration of LPG power sources with paper and other thermally sensitive substrates.
 - a. Temperature rise across the cross-section of PI is modelled to obtain predicted temperatures at the top surface (T_{top}) and bottom surface (T_{btm}) of the PI tape. The predicted temperatures are combined with two reported temperature boundaries ($T_{grphn} = 1775$ K at the top surface and $T_{dmg} = 348$ K at the bottom surface of PI tape). Laser parameters where conditions for LLG can be achieved ($T_{top} > T_{grphn}$ and $T_{btm} < T_{dmg}$) can thus be predicted. These

parameters are experimentally validated across a range of fluence from 0.023 to 0.068 J cm⁻², from 1 to 5000 pulses, and from 50 kHz to 500 kHz.

- b. Parameters for LLG are found to correlate well with experimental predictions. The LPG formed from LLG are characterised with Raman spectroscopy, XPS, FESEM, electrical four-probe testing and laser confocal microscopy. Thermal damage to the substrate is characterised through thermochromic paper at the bottom of the PI tape and confirmed via laser confocal microscopy. The LPG characterised is found to correlate well with other reported works on PG, and no discolouration of thermochromic paper adhered below is observed even under laser confocal microscopy. Together, LPG formation from LLG is validated.
 - c. LPG MSCs are formed from PI directly adhered onto paper and characterised to showcase integrated graphene-paper electronics. Optimised LPG MSC electrodes are tested with cyclic voltammetry and charge-discharge measurements and found to have high capacitive performance even at high scan rates at 100 V s⁻¹. The areal capacitance of the LPG MSC is reported to be 0.428 mF cm⁻² at scan rates of 10 mV s⁻¹ and only reduces by two thirds even at 10,000 mV s⁻¹, similar to results from other reported PG MSCs. These electrochemical results demonstrate that LPG MSCs can be used as site-specific power sources for high-performance self-powered graphene-paper electronics.
 - d. LPG humidity sensors are similarly formed from PI directly adhered onto paper and characterised to showcase integrated graphene-paper electronics. Changes in resistance across the optimised LPG humidity sensors are measured with a source-measure unit and compared with a commercial humidity sensor. The sensor is tested from 4.2% to 76.4% RH for up to three cycles. The humidity sensors are found to repeatably detect humidity with a maximum change of resistance of 4% at maximum RH, with a maximum variation of $\sigma = 0.64$. These results demonstrate that LPG can be used as a simple humidity sensor while protecting the paper substrate below from damage in integrated graphene-paper electronics.
6. A single step femtosecond holographic patterning process using fsLIL is developed to fabricate high-resolution volume phase gratings (VPGs) in unmodified PDMS for tuneable beam steering and spectroscopic applications.
 - a. This patterning induces periodic refractive index modulation (Δn) of 1.95×10^{-4} in the PDMS without post-processing, forming VPGs that work as active

beam steering units and tuneable spectroscopic optical elements. This approach augurs well as a straightforward and single-step method for patterning such elements enabling flexible, stretchable, and compact lab-on-a-chip platforms. Results from this work are critical for future investigations into fsLIL for 3D MB and MSC fabrication.

7.3 Recommendations for future work

The research completed in this thesis on the research and development of fsDLW and fsLIL for 3D power sources lays the groundwork for further investigations in these directions:

- Current fsDLW research into the formation of PG and LPG does not fully utilise the wide range of unique non-linear phenomena that is possible with femtosecond lasers. One non-linear phenomenon, the formation of laser induced periodic surface structures (LIPSS) from fsDLW, has the potential to greatly improve the performance of 3D MBs and MSCs. LIPSS is a phenomenon where self-organised ordered ripples across a material's surface spontaneously forms when the material is exposed above a threshold LIPSS fluence. These structures are not formed from the interference of beams, rather, they self-organise due to as of yet unclear mechanisms. High spatial frequency LIPSS formation in particular is a uniquely femtosecond laser phenomenon, and has been demonstrated to improve the performance of Ni-based cathodes for 3D MBs by up to 2.5 times [262]. LIPSS structures have also been observed on graphene [263]. Therefore, one future research direction would be the formation of LIPSS on PG microstructures to form hierarchal 3D structures with improved surface area and therefore the performance of 3D MBs and MSCs. Patterning could be achieved with the use of an objective lens-based fsDLW system to tightly focus pulses onto the surface of individual PG flakes as depicted in **Figure 7.1**.

Figure 7.1. Schematic for LIPSS formation on fsDLW PG. Patterning is achieved using an object lens capable of tightly focusing femtosecond pulses onto the surface of individual PG flakes.

- The analytical model is currently limited to predicting the formation of PG in general but cannot model more specific differences between different morphologies of PG, which would be useful for further development of PG MBs and MSCs. Therefore, an extension of the model to investigate the effect of predicted temperature for different morphologies of PG would be an important direction for further research. More accurate and direct measurement of temperature during the carbonisation and graphitisation process, possibly through high temporal and spatial resolution thermal imaging would also serve to further refine the accuracy of the temperature model.
- More accurate modelling of PG formation from fsDLW in one dimension and two dimensions could be explored with the accumulated fluence profile (AFP) model. The AFP model is an analytical model which attempts to consolidate various laser process parameters such as scan speed and line overlap into an accumulated fluence value across the written area as schematically shown in **Figure 7.2**. While AFP is originally used to model the formation of LIPSS, the general principles of APF could be translated to fsDLW, to overcome the limitations of the current theoretical model [153]. The current theoretical model for PG formation assumes that no scanning takes place, and all pulses irradiate the same spot. While this approach makes it easier to develop the original model, this difference meant that determination of PG formation across arbitrary 1D and 2D geometries is less accurate. This lowered accuracy is also reflected in the difference between the LLG regime identified for scanning versus spots, as discussed in **Chapter 5**. AFP could be utilised to reconcile these two sets of predictions. An additional advantage to working with AFP is easier adaptation since AFP was originally designed for use with femtosecond lasers. In this manner, the formation of

arbitrarily shaped devices could be more easily optimised.

Figure 7.2. Schematic overview of the accumulated fluence profile (AFP) model. (a) AFP of fsDLW writing where line and pulse overlap is minimal. (b) AFP of fsDLW writing where line and pulse overlap is increased. Each circle represents fluence on one part of the surface, and together these circles make up the AFP. Greater overlap between circles represents a larger accumulated fluence.

- The analytical model developed and applied for LLG could be further improved for more accurate temperature modelling at the bottom surface of PI tape. Improvements could come from additional modelling of ablation effects and other non-linear effects from femtosecond pulse irradiation [107]. Improvement of this analytical model can also be used to identify LLG for other material and laser systems.
- The current performance of PG MB and MSCs could be improved through further optimisation. Different PG morphologies, especially those with greater surface area and a greater degree of graphitisation could be explored. The addition of different additives or use of precursor materials infused with useful additives such as boron to form P or N doped materials could also be explored for 3D MB applications [214]. Increasing the overall volume and amount of PG by optimising the fsDLW fabrication process could also be useful to improve the performance of these MBs. Optimisation can also be achieved through research into PG formation from not only different materials, but different forms of materials as well, including liquids, fibres or even woven fabrics.
- Research is needed to develop or find a better method to measure PG surface area. While BET surface analysis has been widely reported as a method to determine specific surface area, the accuracy of BET for PG materials formed from laser graphitisation cannot be guaranteed. BET can only accurately measure the specific surface area of LPG when removed from the PI precursor. This process is difficult to control, especially since the amount of LPG removed from PI cannot be effectively controlled. Therefore, BET is not the most suitable method to determine specific surface area in this context. One of the alternatives that we are exploring for future work is on alternative methods to determine such as electrochemical surface area (ECSA)

determination [59, 264]. ECSA is a method where surface-limited faradic reactions are utilised to estimate the overall accessible surface area of a porous material. By inducing cyclic reactions where hydrogen adsorption and desorption occurs on active reaction sites, the number of such sites (hence electrochemical surface area) can be determined. ECSA has been utilised in determining the area of graphene materials, making it suitable for use with PG [264]. Furthermore, unlike BET, ECSA can be done in-situ, when eliminates the need to remove PG from the PI precursor at all. ECSA therefore provides an opportunity to determine surface area more accurately for 3D MBs and MSCs from PG.

- Results from fsLIL patterning of PDMS could be used to drive further research into direct patterning of different current collector substrates (Cu, Al) on polymeric substrates. High aspect ratio patterned microstructures can be thus formed directly onto thin, flexible current collectors without the use of expensive and complex photolithography. MB and MSC materials can then be deposited directly on these 3D structures, as schematically shown in **Figure 7.3**.

Figure 7.3. Schematic overview of fsLIL direct current collector (CC) patterning. (a) fsLIL patterning process to form periodic patterns directly on CC through ablation. (b) Full 3D MB/MS after deposition of active materials and second CC layer. Inset: Different layers of material after deposition.

- Further theoretical development and modelling could be done to optimise 3D structures for 3D MBs and MSCs. These patterns must have high contrast and be mechanically stable such that subsequent layers can be deposited on them. This model must also be able to optimise for ion and electron diffusion, which would require insights from other theoretical models such as the Butler-Volmer model for electrochemical kinetics [5]. These improvements in modelling will be done in tandem with further fsLIL set-up optimisation and improvement.
- To further increase the available surface area for high-performance 3D MBs and MSCs, future research could also investigate the combination of fsLIL and fsDLW methods. In this manner the advantages of both methods (deterministic designs and stochastic formations) can be combined to form hierarchal structures which could potentially

increase surface area multiple-fold, similar to how virus-templated structures were combined with etched silicon substrates to multiplicatively increase the available surface area for electrochemical storage in MBs [62].

- Both fsLIL and fsDLW systems are currently limited to patterning materials that are already placed within the patterning area. Fabrication of full MBs and MSCs however, requires many different materials, from other active materials (such as electrolytes or electrode materials) to inactive materials such as current collectors and packaging material. Achieving full fabrication would require the integration of a x-y-z capable material deposition unit, such as a robotic dispensing unit with multiple material deposition heads (shown in **Figure 7.4** with a single dispensing head). Robotic dispensing, alongside other material deposition technologies such as inkjet or aerosol jet printing enable a wide range of printable materials that could even be deposited onto existing electronics if required. When combined with fsDLW and/or fsLIL, the materials that are deposited could also be subsequently cured, sintered or otherwise treated by laser irradiation, thereby achieving fully integrated MB and MSC fabrication.

Figure 7.4. Schematic of a proposed integrated fsDLW system with a robotic material dispenser. The system consists of a femtosecond laser, galvano-scanner, a robotic material dispenser and a control computer.

In summary, the above contributions are envisaged to further the development of scalable and cost-effective fabrication strategies for 3D MBs and MSCs. Development will be achieved through a combination of enhanced control over fabrication with improvements in theoretical

modelling and novel fabrication methods and instrumentation. Together, these developments will result in high electrochemical and capacitive performance for 3D MBs and MSCs fabricated from both fsDLW and fsLIL. **Figure 7.5** in the next page summarises the direction to tackle these recommended objectives.

Figure 7.5. Roadmap summarising the research objectives completed and recommendations for future work. This roadmap summarises the proposed future research direction along with the research contributions made from this research, based on completed research objectives. Current novel contributions of this research work and future work directions are indicated accordingly.

List of Publications

Journal papers

- [1] **Tham, N.C.Y.**, P.K. Sahoo, Y.-J. Kim, V.M. Murukeshan, *Ultrafast volume holography for stretchable photonic structures*. Optics Express, 2019. **27**(9): p. 12196-12212.
- [2] **Tham, N.C.Y.**, P.K. Sahoo, Y. Kim, C. Hegde, S.W. Lee, Y.-J. Kim, V.M. Murukeshan, *Thermally controlled in-situ formation of localised porous graphene for integrated graphene-paper electronics*. Advanced Materials Technologies, 2021. **6**(5): p. 2001156.

Patents

- [1] **Tham, N.C.Y.**, P.K. Sahoo, V.M. Murukeshan, Y.-J. Kim and M.J. Low, *A Methods And An Apparatus For Manufacturing A Porous Graphene Layer Across A Precursor Material Layer On A Substrate Through Thermally Localised Laser Graphitisation*, Singapore Application No. 10202010197X, Patent pending.

Conference proceedings

- [1] **Tham, N.**, Y.-J. Kim, and V.M. Murukeshan, *Multi-beam interferometric patterning in optically transparent materials*. in *Fifth International Conference on Optical and Photonics Engineering*. 2017. Singapore: Proceedings of SPIE.
- [2] **Tham, N.C.Y.**, V.M. Murukeshan, and Y.-J. Kim., *Line Morphology Investigation of Laser Induced Graphene from Polyimide for 3D Printed Electronics*. in *3rd International Conference on Progress in Additive Manufacturing*. 2018. Singapore.

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Appendices

Appendix A: Overall femtosecond laser set-up

A.1 Femtosecond laser and lab set-up

The overall femtosecond laser set-up used in this research work is custom built and shared by the authors research group. The whole set-up is constructed on a large 1.5 x 2.5 m optical table and consists in total of one high-powered femtosecond laser (Amplitude Systemes Satsuma HP Yb fibre laser) with a custom ordered output coupler capable of generating pulses in the second harmonic (515 nm) and third harmonic (343 nm) from the fundamental wavelength (1030 nm). Each of these wavelengths have a separate output from the coupler, each with their own separate beam line. These beam lines lead to three separate fabrication platforms: galvano-scanners based fsDLW systems, an objective lens and x-y motorised stage fsDLW system, and a two-beam fsLIL set-up, the development of which was detailed in **Chapter 3**. The femtosecond laser, output coupler and three fabrication platforms are all protected from the outside environment by a custom designed hard cover. A laser control software, Eastern Logic's MarkingMate is used to control the overall system. **Figure A.1** on the next page shows the overall arrangement of the different components.

Figure A.1. Arrangement of the femtosecond laser system's components. (a) Image of the femtosecond laser set-up from the femtosecond laser. The two-beam femtosecond laser interference lithography (fsLIL) set-up is in the top right of the image, the galvano-scanner femtosecond direct laser writing (fsDLW) set-up is in the top left and the objective lens and motorised scanning stage fsDLW set-up is to the left of the galvano-scanner set-up (hidden). The dotted rectangle represents the view for (b). (b) Image of galvano-scanner (right) and objective lens (left) fsDLW set-ups.

The schematic in **Figure A.2** depicts the different beam paths to the various fabrication platforms for the three wavelengths. The only wavelength that leads to the two-beam fsLIL set-up is 343 nm, and two separate galvano-scanners are used for 343 nm and 515 nm & 1030 nm together respectively.

Figure A.2. Beam path schematic from the femtosecond laser output coupler. Each of the output wavelengths are depicted in their respective colours: blue (343 nm), green (515 nm) and red (1030 nm). RM: Removable mirror on indexing mount.

The specifications of the femtosecond laser used are shown in below.

Amplitude SYSTEMES			Certificate of Conformance					
IR	Laser Parameters		Unit	Target		Measurement		Fulfilled
				500 kHz	2 MHz	500 kHz	2 MHz	
	*Energy per pulse		μJ	≥ 20	≥ 5	21.0	5.3	☒ yes ☐ no
	*Average power		W	≥ 10	≥ 10	10.5	10.6	☒ yes ☐ no
	Center wavelength			1030 +/- 5		1031.3	1031.8	☒ yes ☐ no
	Bandwidth FWHM		nm	≤ 10		8.0	9.1	☒ yes ☐ no
	*Pulse duration		fs	< 500		230	220	☒ yes ☐ no
	Pulse energy over 12h	Average	μJ	> 20	N/A	21.1	N/A	☒ yes ☐ no
		RMS	%	< 2		0.15	N/A	☒ yes ☐ no
	Polarization ratio		-	> 100:1		2040:1		☒ yes ☐ no
	M²	M²x	-	< 1.20		1.16		☒ yes ☐ no
		M²y				1.10		☒ yes ☐ no
	Beam diameter	W0x	mm	2 +/- 0.5		2.31		☒ yes ☐ no
		W0y				2.33		☒ yes ☐ no
	Beam ellipticity			< 13%		0.8		☒ yes ☐ no
Astigmatism		%	< 50%		22		☒ yes ☐ no	
Waist ellipticity			< 13%		6.0		☒ yes ☐ no	
Pointing stability		μm	< 150		x:25	y:32	☒ yes ☐ no	
SHG	Laser Parameters		Unit	Target		Measurement		Fulfilled
				500 kHz		500 kHz		
	Energy per pulse		μJ	≥ 8		10.4		☒ yes ☐ no
	*Average power		W	≥ 4		5.2		☒ yes ☐ no
	Pulse energy over 12h	Average	W	≥ 8		10.3		☒ yes ☐ no
		RMS	%	< 2		0.53		☒ yes ☐ no
	Beam diameter	W0x	mm	2.0 +/- 0.5		2.34		☒ yes ☐ no
		W0y				2.23		☒ yes ☐ no
Beam ellipticity		%	< 13%		4.4		☒ yes ☐ no	
THG	Laser Parameters		Unit	Target		Measurement		Fulfilled
				500 kHz		500 kHz		
	Energy per pulse		μJ	≥ 3		4.5		☒ yes ☐ no
	*Average power		W	≥ 1.5		2.3		☒ yes ☐ no
	Pulse energy over 12h	Average	μJ	≥ 3		4.5		☒ yes ☐ no
		RMS	%	< 2		0.27		☒ yes ☐ no
	Beam diameter	W0x	mm	1.5 +/- 0.5		1.67		☒ yes ☐ no
		W0y				1.71		☒ yes ☐ no
Beam ellipticity		%	< 13%		2.5		☒ yes ☐ no	
* If laser concerned with LIGLO ref.728 : attach the certificate								
This device fulfills the acceptance criteria @ AS and is therefore ready for shipment:					Kévin GEERAERT - 05/07/2016 - KGE			
☒ yes ☐ no								

Figure A.3. Femtosecond laser specifications. Specifications listed on the Certificate of Conformance are provided by the manufacturer after installation and testing.

A.2 Laser design software methodology: MarkingMate

To add the “wings” described in **Chapter 3** into designs, the following methodology is used, based off MarkingMate. First, an arbitrary design (for example, an in-plane MSC) is drawn in any 2D or 3D modelling software. At this stage, the wings may or may not be added into the design, depending on the experiments to be performed and the complexity of the wings. If one of the parameters under study is the scanning direction, wings would not be added at this stage, otherwise they would. The overall dimensions and position of the wings follows the description in **Chapter 3**. This design exists only as an outline at this stage.

Next, the design is exported from the modelling software as a “.dxf” and imported into the MarkingMate software. At this stage, wings would be added if they otherwise have not been, and the separate wings and design are <Combined (K)> in MarkingMate.

Finally, the combined design is shifted to the correct position in the program, the laser and process parameters chosen, and the design written into the precursor material as described in **Chapter 3**. The following flow chart in **Figure A.4** summarises the whole process.

Figure A.4. MarkingMate design methodology. Blue items are done in the chosen 2D/3D software, and green items are done in MarkingMate.

Appendix B: Theoretical model implementation

B.1 Theoretical model implementation in MatLab® code

The analytical theoretical model developed to predict PG formation is implemented as MatLab® code. Several different sets of code are implemented differently to showcase different sets of information. All these sets of code implement the same equation, but with main differences in presenting the data. Some of the shared code blocks are shown in **Figure B.1**.

```

%initialise laser and unchanged material properties

alpha = 2.1246e5;      %absorption coefficient of PI in m-1
row = 1.42e3;          %density of PI in Kg/m3
R = 0.082;             %Reflectivity of PI at desired wavelength
r = 0e-6;              %position coordinate in meter
Z= 0e-6;               %depth in meter
wd = 46e-6;            %beam diameter in meter
w = wd/2;              %beam radius in meter
delta = 1/(w*alpha);   %characteristic absorption depth
lz = 1/alpha;           %absorption depth
l = lz/2;
f = 250e3;              %repetition rate
N = 1;                  %no. of pulses
tL = 1./f;              %pulse gap in s
tf = N.*tL;             %time (in s) exactly at the last pulse
int = 1e-10;            %interval
td = 1e-3;              %duration
t = 0e-15;              %start time
T = 300;                %initial temp
t_a = 0;

%define figure axes and labels

legend('F = 0.0233 Jcm^-^2', 'F = 0.0455 Jcm^-^2', 'F = 0.0683 Jcm^-^2');
ay = gca;
ay.FontSize = 10;
ay.YAxis.Exponent = 0;
xlabel('Time (ms)', 'FontSize', 12, 'FontWeight', 'bold', 'Color', 'k');
xticks([0 0.25 0.5 0.75 1]);
xticklabels({'0', '0.25', '0.50', '0.75', '1.00'});
ylabel('Temperature (K)', 'FontSize', 12, 'FontWeight', 'bold', 'Color', 'k');
legend('show');
axis([-0.05 1 300 390]);

%export high resolution image of figure

set(gcf, 'Position', [100, 100, 250, 300])
set(gcf, 'Color', 'w');
set(gca, 'Color', 'none');
export_fig singlePulserev002.png -transparent -m2 -painters

```

Figure B.1. Shared code blocks for initialisation and formatting. From top: code block to initialise fixed laser and material parameters, code block to define figure axes and labels, and code block to export high-resolution images.

The values for N , f and F change according to the information to be depicted.

The other main shared block of code implements the theoretical model (**Figure B.2**).

```

%initialise temperature dependent material properties

for t=-1e-4:int:td %time at the end of last pulse %10:10:5000
tL = 1./f; %pulse gap in s
tf = N.*tL; %time (in s) exactly at the last pulse
Cp(1) = 0.96e3; %initial specific heat capacity of PI in
J/(Kg.K)
Tp(1) = 300; %initial temperature of pulse
k(1) = 0.155; %initial thermal conductivity
D(1) = 1.137e-7; %initial thermal diffusivity in m2/s
Tpeak(1) = (alpha.*(1-R).*F)./(row.*Cp(1));
%maximum temperature (K) increase by one
laser pulse
%run equation for no. of pulses

for n=1:1:N %number of
pulses
t1=t-((n-1)*tL);
tow1=(4*D(n)*t1)./(w^2);
brak=alpha.^2.*D(n)*t1;
tow2=real(sqrt(brak)-(Z./(2.*sqrt(D(n)*t1)))); %only for real
terms
tow3=real(sqrt(brak)+(Z./(2.*sqrt(D(n)*t1))));
T_r=exp((-1.*r.^2)./(w.^2).*(1+tow1)); %radial term
T_z=exp(brak).*(exp(-alpha.*Z).*erfc(tow2)+exp(-
alpha.*Z).*erfc(tow3)); %axial term

deno=2.*sqrt(pi)*(1+tow1);
Tpeak(n+1)=(alpha.*(1-R).*F)./(row.*Cp(n));
Tp(n+1)=T_r.*T_z.*Tpeak(n+1).*heaviside(t1)./deno;
Tp(n+1)=Tp(n)+Tp(n+1);
if Tp(n+1)<=900
k(n+1)=100*(1.55e-3+6e-4*((Tp(n+1)-300)/400)-1.7e-
4*((Tp(n+1)-300)/400).^2); %change in conductivity (W/m/K)
of PI from Kuper & Brannon
elseif Tp(n+1) > 900 && Tp(n+1)<= 1775
k(n+1) = k(n); %keep maximum thermal
conductivity change
else
k(n+1) = 0.7; %thermal conductivity of
graphene/graphite
end
if Tp(n+1)<=900
Cp(n+1)=1000*(0.96+1.39*((Tp(n+1)-300)/400)-0.43*((Tp(n+1)-
300)/400).^2);
D(n+1)=k(n+1)./(row*Cp(n+1)); %keep maximum diffusivity
change
else
Cp(n+1)= Cp(n); %keep maximum specific heat
capacity
change
D(n+1)=k(n+1)./(row*Cp(n+1));
end
end
end

```

Figure B.2. Shared code blocks for model implementation. Includes initialisation of temperature dependent material properties.

Depending on the information required, other parts of the code will change. For example, for single pulses, multiple values of F are taken, while for multiple pulses, different values of f and N are taken for the same total amount of time. These different code blocks are shown in **Figure B.3**.

```
%for single pulse: run code for equation for number of fluence
values in array F

for F = [0.0233e4 0.0455e4 0.0683e4]

    imax = (td-(-1e-4))/int; %counter for number of fluence values
    i = 1;

    ...

end

%for multiple pulses across different repetition rates: run code
for equation for number of rep rate values in array f, but change
manually

for f = [50e3]; %500e3 250e3 100e3
    tL = 1./f; % pulse gap in s
    imax = (td-(0))./int; %counter for number of fluence values
    i = 1;
    if f == 500e3
        N = 1000;
    elseif f == 250e3
        N = 500;
    elseif f == 100e3
        N = 200;
    else
        N = 5000;
    end
    tf = N.*tL; %time (in s) exactly at the last
pulse
    tLast = tf + 0e-6; %time (second)somewhere after the last pulse
elapsed

    ...

end
```

Figure B.3. Separate code blocks for depicting different information. From top: code block for single pulses, code block for multiple pulses and different repetition rates for the same period. The code block that implements the model fits into the for loop at the ellipses.

To generate temperature predictions for the whole range of parameters N (1 to 5000), F (0.023 J cm⁻² to 0.068 J cm⁻²) and f (50 to 500 kHz), the above code blocks can then be expanded to loop through each of these parameters at the top surface. The time at which the temperature is taken is fixed at exactly the temperature rise due to the last pulse. After this array of temperatures predictions (based on N and F) is obtained for each f , these values can then be

compared with the Raman spectroscopic results for the same values of f , F and N . The results of this comparison are thus shown in **Figure 4.3**.

Appendix C: Localised laser graphitisation (LLG)

C.1 Modified theoretical model implementation in MatLab® code for localised laser graphitisation (LLG)

Extending the theoretical model in code to investigate the temperature rise across the cross-section of PI is relatively straightforward. Since the original code and formulation already includes a term for temperature at depth and radius, therefore calculating the temperature rise is simply a matter of calculating temperature rise at each depth section for a fixed radius. One additional complexity that has to be managed however, is the change in material parameters at the interface of the PI film and silicone adhesive. Since calculation only takes into account material properties, any changes in temperature due to this interface is not considered. The cross-sectional temperature information can thus be calculated and shown from the code block in **Figure C.1** in the next page.

Similarly, to calculate temperature predictions across both the top and bottom surfaces of the PI tape, z can be set at $65\text{ }\mu\text{m}$, and the temperature predictions across the different parameters can be calculated for both surfaces. These results can then be compared with the Raman spectroscopic results and the thermochromic results to identify the localised laser graphitisation (LLG) regime, as shown in **Figure C.2** and **Figure C.3** in the following page consolidates the raw images obtained under laser confocal microscopy that enabled the validation of the predicted LLG regime. Images from spot as well as scanned LPG are obtained.

```

%run equation in radial and axial directions for cross-section

i1 =1; %initialise counter for r
j1 =1; %initialise counter for z
sizeofrow = (w+w)/ 1e-6; %counter for r values
sizeofcol = (65e-6 - 0)/1e-6; %counter for z values
while (i1<sizeofrow)
    for r=-w:1e-6:w
        %range of values of radius r across
        %beam diameter wd
        %resolution 1 um

        while (j1<sizeofcol)
            for Z=0:1e-6:65e-6
                %range of values of z from 0
                % (surface) to 65 um (end of
                % adhesive)
                %resolution 1 um

                Tp(1)=300; %initial temperature
                n = 1; %no. of pulses
                if Z<= 25e-6
                    Cp(1) = 0.96e3; %initial specific
                    % heat capacity of PI
                    % in J/(Kg.K)
                    %initial thermal

                    conductivity k(1) = 0.155;

                    D(1)=1.137e-7; %initial thermal
                    % diffusivity in m2/s

                else
                    Cp(n) = 1.46e3; %specific heat
                    % capacity of silicone
                    % adhesive

                    k(n) = 0.2; %thermal
                    % conductivity of
                    % silicone adhesive

                    D(n) = k(n)./(row_sa*Cp(n)); %thermal diffusivity
                    % of silicone adhesive

                end
                ...

                T=Tp(n+1);
                Tcal(i1,j1) = T; %store temperature

                value R_value_store(i1,j1) = r;

                %store temperature
                % value in array for
                % depiction in r

                Z_value_store(i1,j1) = Z;

                %store temperature
                % value in array for
                % depiction in z

                j1 = j1+1;
            end
        end
    end
end

```

Figure C.1. Code block to calculate temperature rise within PI and silicone adhesive cross-section.
As before, the code block that implements the model fits into the for loop at the ellipses.

Figure C.2. Thermochromic paper results for validation of the LLG regime. (a) Results for 50 kHz, (b) 100 kHz, (c) 250 kHz and (d) 500 kHz obtained under laser confocal microscope at 5X magnification.

Figure C.3. Thermochromic paper samples. (a) Peeled and unpeeled samples for spot LPG. (b) & (c) Peeled and unpeeled samples for scanned LPG with wings.

C.2 Measurement and calculation of relative humidity (RH) data

Relative humidity (RH) measurements are calculated from stepwise measurements of resistance response versus reference relative humidity. As the originally obtained data contained many extraneous frequencies, fast Fourier transform (FFT) filtering is used to filter the data. The filtered data is then used to calculate the normalised changes in resistance over relative humidity. At each set step of 10 % RH, the filtered values are taken for constant RH. As an example, this means that all the filtered values in the green shaded region in **Figure C.4** are taken to be values for 50% RH. The resistance and standard deviation values are calculated from these filtered values from each RH step.

Figure C.4. Stepwise relative humidity data from LPG humidity sensor. The blue line represents data collected from the reference humidity sensor, the grey line represents data collected from the LPG sensor, and the green line represents the RH data from the LPG sensor after fast Fourier transform (FFT) filtering. This stepwise data is used to calculate the normalised change in resistance over relative humidity. The shaded region marks the normalised resistance values taken for 50% RH.

Appendix D: UV-Vis spectrum of PDMS

D.1 UV-Vis absorbance and transmission spectrum of PDMS

The UV-Vis absorbance and transmission spectrum of PDMS is shown in **Figure D.1** below.

Figure D.1. UV-Vis absorbance and transmission spectrum of PDMS. Data is obtained from 200 nm to 1000 nm.