Novel Fast Fabrication of Nano-Structures for Sensor and Flexible Polymer Electronics

by

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Abstract

Applications of engineered surface nano-structures span several domains. For emerging technologies such as flexible electronics and low cost sensors, the ability to produce large areas of surface nano-structures at high volume economically, can help realize several applications. One approach of achieving high volume production of surface nano-structures economically and reliably is by replication from a master stamp or template. Conventional methods in producing master stamps rely on the lengthy use of scanning-types of patterning tools, such as electron beam lithography and focused ion beam. The duration and cost of patterning limits the practicality in producing large area masters.

In this thesis work, a novel method to achieve faster fabrication of master stamps containing original surface nano-structures is proposed and demonstrated. This method creates initial circular patterns of smaller dimensions than the final desired, then subsequently enlarges to the full size using lower cost processes. The target structure size range between 150 nm to 500 nm, which is relatively lengthy to pattern using conventional focused ion beam or electron beam lithography tools, compared to sub 100 nm spot patterns. However, the time required to pattern the nano-structures through this method is reduced by 3 X compared to the conventional, and can be further optimized to find additional cost savings. The throughput improvement is particularly noticeable for nano-structured regions larger than 1 cm². The process is correspondingly valuable for users who do not have access to the most advanced, latest and fastest, patterning tools. Exemplar replication techniques such as polymer embossing, casting, and electroforming are also demonstrated and discussed. Analysis on both the original masters and the replicated samples show good pattern transfer and excellent yield. A selected application example on an integrated sensor containing nano-optics is discussed in detail. The nano-optics sensor structures are produced at lower cost than the traditional, while still exhibiting useful sensitivity. This specific application example validate the utility of the improved master stamp fabrication process towards enabling high volume production of large area nano-structures for end applications economically.
This thesis identifies the background science and challenges to current technology, discusses the motivation and objectives, methodically contemplates a solution, demonstrates the novel master stamp fabrication process, discusses extended replication techniques, examines the produced structures, and provides validating application examples. Selected portions of the work is further shared with the community of scientist and engineers through journal and patent publications. The thesis report provides additional insight on the concepts, techniques, and analysis.

Keywords: Electron Beam Lithography; Flexible Electronics; Integrated Sensors; Nano-Structures; Nano-Stamps; Polymer Electronics
Dedication

I dedicate this work to my father. His sharp acumen and tenacious work ethics is an inspirational model. Having never had the chance to pursue an extended advanced education, in favour of joining the work force to support his family, he preached the added values in life in higher learning. The young men and women of today’s urban world are often blessed with the choice of undertaking quality education. This luxury should be met with the awareness of constructive uses of the knowledge obtained, to ourselves, those around us, and the society we live in.
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I wish to acknowledge the Natural Sciences and Engineering Research Council of Canada for supporting my training through their various graduate scholarships and industrial partnered internship programs. I am also thankful for all the collaborative efforts, of great and small, from my lab mates over the years. They’ve not only added value to the incremental work, but more so, they’ve added life to the process of this work itself. Last, but certainly not least, I deeply appreciate the unique and challenging research environment that my senior supervisor has provided. It is a journey rare and rewarding in its own way. It is an one of a kind learning opportunity to be cherished and built-on for the span of a career.
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## Acronyms and Glossary

<table>
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<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>2D</td>
<td>2-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>3-dimensional</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current, current flow</td>
</tr>
<tr>
<td>A/D</td>
<td>Analog-to-digital, signal conversion</td>
</tr>
<tr>
<td>anisotropic</td>
<td>Not isotropic, directional</td>
</tr>
<tr>
<td>aperiodic</td>
<td>Not periodic, non repeating</td>
</tr>
<tr>
<td>DB</td>
<td>Dual beam</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current, current flow</td>
</tr>
<tr>
<td>DRIE</td>
<td>Deep reactive ion etch</td>
</tr>
<tr>
<td>DUV</td>
<td>Deep-UV, UV light in the lower wavelength spectrum of UV, typically below 300 nanometers</td>
</tr>
<tr>
<td>EBL</td>
<td>Electron beam lithography</td>
</tr>
<tr>
<td>EOT</td>
<td>Extraordinary optical transmission</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>IPMC</td>
<td>Ionic-polymer-metal-composites</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared, refers to the region in the electromagnetic spectrum where the wavelength is just beyond the visible light spectrum colour red</td>
</tr>
<tr>
<td>isotropic</td>
<td>In all directions</td>
</tr>
<tr>
<td>laser</td>
<td>Light amplification by stimulated emission radiation</td>
</tr>
<tr>
<td>LIL</td>
<td>Laser interference lithography</td>
</tr>
<tr>
<td>m</td>
<td>Meter, measure of distance (SI unit)</td>
</tr>
<tr>
<td>MCU</td>
<td>Microprocessor unit</td>
</tr>
<tr>
<td>metamaterial</td>
<td>Artificial materials engineered that may not be found in nature</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer, one millionth of a meter</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro-electrical-mechanical systems</td>
</tr>
<tr>
<td>MIM</td>
<td>Metal-insulator-metal; a substrate architecture referring to metal layered on both sides of an insulator</td>
</tr>
<tr>
<td>NEMS</td>
<td>Nano-electrical-mechanical systems</td>
</tr>
<tr>
<td>Nanoholes</td>
<td>Depressed, hole-like structures with a diameter in the nanometer range</td>
</tr>
<tr>
<td>Nanopillars</td>
<td>Protruding, pillar-like structures with a diameter in the nanometer range</td>
</tr>
<tr>
<td>NIL</td>
<td>Nano imprint lithography</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer, one billionth of a meter</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
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<tr>
<td>OLED</td>
<td>Organic light emitting diodes</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaics</td>
</tr>
<tr>
<td>periodic</td>
<td>Repeated at regular intervals, of a recurring pattern</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate, plastic</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate, plastic</td>
</tr>
<tr>
<td>PMGI</td>
<td>Polymethylglutarimide</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene, plastic</td>
</tr>
<tr>
<td>PR</td>
<td>Photoresist</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene, plastic</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride, a piezoelectric film</td>
</tr>
<tr>
<td>R2R</td>
<td>Roll-to-roll production, a concept in patterning soft material surfaces at relatively low cost</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive ion etch</td>
</tr>
<tr>
<td>RIU</td>
<td>Refractive index unit</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>SOI</td>
<td>Silicon-on-insulator; a substrate architecture that refers to silicon-insulator-silicon layering</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface plasmon resonance</td>
</tr>
<tr>
<td>sputtering</td>
<td>A process whereby atoms are ejected from a solid material by energetic particles</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet, ultraviolet light, referring to light with wavelength in the range of 10 to 400 nanometers</td>
</tr>
<tr>
<td>X-ray</td>
<td>A range of electromagnetic radiation with wavelength between 0.01 to 10 nanometers</td>
</tr>
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1. Introduction to Surface Nano-Structures

1.1. What Are Surface Nano-Structures

Nano-structures are structures that have dimensions in the range of nano-meters (1/1,000,000,000\textsuperscript{th} meter). They can be composed of any material and take any shape. They can exist independently or collectively to form a larger functional structure. Naturally occurring nano-structures include cellular lipid bilayers (10 nm), biological viruses (100 nm), and mud colloids (<1 µm) to name a few. Nano-structures are nearly the smallest structures that can be resolved with current imaging technologies, for example, using scanning electron microscopes (SEM) [1][2]. Figure 1-1 gives a perspective on the dimensions of some well-known naturally occurring biological structures and engineered structures spanning across the length scale from the nanometer range to the meter range.

As science and engineering technologies advance, the human ability to synthetically create small structures consequently develops. Engineered materials and metamaterials consisting in-part or wholly with nano-structures, span a variety of applications and industries. Engineered nano-structures can be periodic or aperiodic. They can be further categorized into surface-existing, independent or free-standing, or bulk-assembled types. This thesis work focuses particularly on surface nano-structures and their applications.
Figure 1-1: Comparison of size for a few exemplar naturally occurring biological structures and engineered structures spanning across the length scale from nanometer to meter.

Figure 1-2 shows a small section (approx. 5 μm by 5 μm) of an engineered nano-structured quartz stamp. The nano-structures have pillar-like conical shape. The pillars extend out-of-plane, standing at approximately 400 nm tall, and are arranged in a square lattice along the surface plane spaced 600 nm apart from each other. Protruding surface nano-structures are particularly useful in replicating inverse copies of itself on soft materials, conceptually much like stamping; in this case, the inverse structures are arrays of nano-sized holes, or indentations into the substrate surface. This replication process can be repeated for mass production.
Figure 1-2: SEM image (tilted side view at 52°) of a small 5 µm by 5 µm surface segment of a quartz stamp showing its protruding quartz nanopillar structures with conical shape and arranged in a square lattice. This example is produced using the techniques developed in this work.

Figure 1-3 further shows a small section of another nano-structured quartz surface. This surface contains nanoholes arranged in a periodic square lattice. The indented structures can also be applied as a replication template. Figure 1-4 shows surface nano-structures constructed in a multi-layered arrangement, where a layer of waffle-shaped metal shell is stacked on top of quartz nanopillars.

Whether they are protruded, indented, or stacked, the uniquely arranged surface nano-structures have many useful applications. However, despite their exciting applications, engineered nano-structures can be costly, time-consuming, and difficult to produce. Developments in nano-structure fabrication over the past twenty years have incrementally added techniques for large volume production of surface nano-structures [3]. The use of nano-structured stamps, such as that shown in Figure 1-2, is one of the cornerstone methods for nano-structure manufacturing. Hence, improving the fabrication of these nano-structured original master stamps brings value to the community of science and engineering that is concerned with surface nano-structured devices.
Figure 1-3: SEM image (top view) of a small 3 µm by 3 µm surface segment of a quartz template showing nanohole structures arranged in a square lattice. This example is produced using the techniques developed in this work.

Figure 1-4: SEM image (tilted side view at 52°) of a multi-layer nano-structure arrangement showing nanopillars with a portion having waffle-shaped metal layer (yellow annotation colouring) stacked on top. This example is produced using the techniques developed in this work.
1.2. Uses of Surface Nano-Structures

Applications of engineered surface nano-structures can be found in several areas of technologies, and are quite often interdisciplinary. Table 1-1 gives a brief list of technology applications that involve the use of surface nano-structures. The selected applications surveyed represents only a small population of the extensive emerging uses of nano-structures across all disciplines of science and engineering, however, it provides a basic understanding of the genre of relevant nano-structures in this study. The summary presents the associated nano-structures with each application and lists an aggregate of materials in which the structures are patterned on or made of.

Bio-chemical sensing based on surface plasmonic resonance (SPR) can provide a label-free approach to detection and measurement of the analyte species. Recent demonstrations of SPR based sensing using surface nano-structures include primarily 2-dimensional periodic nanohole arrays on thin metal films [4]-[10]. The nanoholes penetrate through the metal films and have typically smaller diameters than the wavelength of visible light. The most basic periodic arrangement include square lattices with spacings below 1 µm, much like that shown in Figure 1-3. Among all applications of surface nano-structures in health related sciences, SPR based bio-chemical sensing using nano-structure arrays to facilitate detection is one of the most widely studied. This subject will be examined more in-depth as a demonstrative case for applications of the nano-structures and methods developed in this work.

Photonic surface waveguides and photonic cavities are increasingly being explored and applied in optical computing and communications. These planar photonic structures contain high aspect ratio nanohole structures arranged in continuous periodic arrays with voids or irregularities inserted within to act as light-guiding structures [11],[12]. Light is directed along the plane of the nano-patterned substrate and manipulated according to the designed path, confinement, or emitter. The substrate materials include a variety of semiconductor and dielectrics based on their photonic band gap properties. The dimensions of the holes and the periodic spacings are designed to isolate or reject specific photonic bands in order to form the waveguide or resonant cavity structures. A particularly unique and lesser-known unconventional
application is the use of these photonic waveguides and cavities in the sensing of mechanical deformation [13].

Surface nano-structures also find applications toward the enhancement of organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs). Nano-cavity arrays of various shapes can be patterned on the electrode surface of OLEDs or added on top of the device as an external layer to improve the illumination or reliability and cost [14]-[16]. Similarly, 2-dimensional periodic nanohole or nanopillar arrays patterned into or on top of the electrode surfaces of OPVs can increase efficiencies [17],[18]. Typically, the dimensions of these surface nano-structures are below 1 µm, and mostly within the wavelength of visible light to generate the desired optical effects in the colour spectrum.

Applications of surface nano-structures as metamaterial thermal emitters also require periodic patterns. Nano-structures of various shapes such as square or circular indentations on silicon or tungsten based substrates can be designed to emit or reflect at specific wave bands as tuned black body emitters [19]-[23]. As thermal emitters, the periodic nano-structures are spaced in the 1 to 2 µm range, corresponding to the wavelength of near-IR electromagnetic waves.

Slightly more complex surface nano-structures can form dry adhesive surfaces mimicking the skin of some climbing reptiles. Tall pillar-like nano-structures containing enlarged tops, like that of mushroom or nail caps, can be moulded on the surface of soft silicone and rubber materials to texturize the surface such that the surfaces forces are sufficient to support useful loads [24]-[27].

Colour displays can be created with single or multiple layers of surface nano-structures where specific lattice and spacings correspond to different reflected or transmitted lights in the visible spectrum. Examples include high colour definition using nano-gratings patterned on a MIM of Al-ZnSe-Al [28], and tunable colour pixels using silica nano-spheres distributed evenly across a surface [29]. The planar dimensions of the surface nano-structures are again below 1 µm, and mostly within the wavelength of the visible light spectrum, however, several stacked layers of these surface nano-structures can achieve more desirable optical effects.
Finally, 3-dimensional photonic crystals for diode laser cavities can be created on the surface of dielectric substrates. These tailored photonic crystals can provide unique photonic bandgap characteristics unavailable through unmodified materials, and can be more easily integrated with semiconductor light emitting diodes [30]-[33]. The 3-dimensional crystals are mostly created by sequential patterning and stacking of the desired nano-structures, or patterning deep into the substrate through masks or templates.

Table 1-1: Brief list of technological applications involving the use of surface nano-structures, giving summary of the nano-structure shapes and arrangements applied, materials on which the structures are patterned onto, and research development reference examples.

<table>
<thead>
<tr>
<th>Application</th>
<th>Nano-Structure Shapes/Arrangement</th>
<th>Materials</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photonic surface waveguides and cavities</td>
<td>Continuous periodic nanoholes of high aspect ratios with the waveguide or cavity patterns situated within the arrays; size: various, depending on light wavelength of interest</td>
<td>Substrate including SOI: Si-SiO$_2$-Si; SiC; SiN, GaN, GaP, GaAs, etc.</td>
<td>Tokushima 2000 [11] Yamada 2011 [12] Tung 2011 [13]</td>
</tr>
<tr>
<td>Surface plasmon enhanced organic photovoltaics</td>
<td>Primarily 2-dimensional periodic nanohole or nanopillar arrays on device electrode surface; size: 500 nm to 1 µm</td>
<td>Electrodes including ITO, Al, etc.; additional pillar structures including Cd based types</td>
<td>Fan 2009 [17] Menezes 2010 [18]</td>
</tr>
</tbody>
</table>
### 1.3. Approaches to Building Surface Nano-Structures

The fabrication of surface nano-structures can be examined under two fundamental approaches: 1) a bottom-up approach where nano-scale structures are assembled together; 2) a top-down approach where nano-scale structures are patterned onto surfaces of bulk materials. A combination of both bottom-up and top-down approaches can also be used in conjunction to form possibly more advanced structures. Figure 1-5 depicts the relationship and examples of such approaches.

<table>
<thead>
<tr>
<th>Category</th>
<th>Description</th>
<th>Substrates</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomimetic dry adhesive surfaces</td>
<td>3-dimensional nanopillar like structures with enlarged caps (e.g. mushroom or nail caps); size: various</td>
<td>Soft polymers including silicones and rubbers</td>
<td>Sameoto 2008, 2012 [25][27] Krahn 2011, 2012 [24][26]</td>
</tr>
<tr>
<td>Colour displays</td>
<td>Periodic gratings, arrays of nano-spheres, etc.; size: below 1 µm</td>
<td>Substrate for one instance includes MIM: e.g. Al-ZnSe-Al; another example utilizes silica nano-spheres and sol-gel</td>
<td>Xu 2010 [28] Arsenault 2007 [29]</td>
</tr>
</tbody>
</table>
In the bottom-up approach, atomic and molecular scale assembly collectively form larger functional structures. For many cases in this approach, large-area assembly of nano-structures is relatively fast compared to the top-down approach, and at lower costs. Examples of the bottom-up approach include 2-D self-assembly of the nanospheres [34],[35], and 3-D ordered stacking of these nanospheres [36]-[38]; these nanosphere can be composed of metals, colloids, polymers, and proteins. However, inherent to most bottom-up methods for “growing” nano-structures, the propagation of errors during assembly renders the methods defect prone. Further, most assembly methods for the bottom-up approach only allow a single periodic and repeating pattern to be produced across the entire featured area [39],[40].

In contrast, the top-down approach relies on the direct patterning of nano-scale geometries on material surfaces. The methods under this approach provide precise registration of surface structures. The patterns can contain complex artwork that are not necessarily periodic or repeated across the entire featured area. Some examples of “original” pattern registration include the use of focused ion beam (FIB) tool [41],[42], electron beam lithography (EBL) [43]-[46], and laser interference lithography (LIL) [47],[48]. While the initial original patterns of nano-structures are often time-consuming and expensive to generate, once a master design is produced, large volume replication can take place through methods such as nano-imprint-lithography (NIL) [49]-[57],

Figure 1-5: Relationship and examples of the two fundamental approaches (bottom-up, top-down) to surface nano-structure fabrication.
templated ink-printing [58],[59], direct embossing [60], soft casting [61],[62], phase-shift lithography [63], X-ray or deep-UV lithography, and patterning via shadow masks (nano-stencils) [64], to name a few. Some of the additional processes involved in realizing surface nano-structures in the top-down approach include: physical vapour deposition and electrodeposition for addition of thin film material; reactive-ion-etching (RIE) and wet chemical etching for removal of material.

1.4. Motivation and Objectives of Research

World technologies that involve surface nano-structures are becoming a more integral part of the billion-dollar consumer, medical, and energy markets, rather than just outer-space exploratory projects. Several popular visions for advancement in electronics for these markets contemplate large area, ubiquitous, or disposable devices to popularize exponentially. However, some of the key enabling factors in realizing these devices include low cost production, sustainable materials, and well-engineered integration that are often lethargic impediments. Sensors and flexible polymer electronics are two areas of technology that propel these markets, and make excellent candidates in demonstrating the utility of nano-structures through practical engineering in overcoming the afro-mentioned fundamental challenges.

The top-down approach in producing surface nano-structures, allows precise and fast replication, enabling large volume production that are otherwise difficult to accomplish. However, every replication method inherently requires a master stamp or template containing “original structures” as the source for replication. Most of the current methods in producing master stamps are largely time-consuming and expensive. Although flood-types of original pattern generation (e.g. LIL) are relatively faster, they are very limited in design pattern complexities. It is evident that the nanotechnology community would benefit immensely by gaining new processes in producing original surface nano-structures that are faster than the conventional, while still allowing for complex patterns. The ability to produce master nano-structure stamps at a higher throughput will translate to lowering costs in large volume replication production of nano-structures, which in turn engages applications previously unattainable due to limited size and costs of master stamps.
The goals of this research thus follow the pragmatic approach to addressing this challenge by:

- **Examining** the conventional methods in producing original nano-structures, such as EBL, FIB, and LIL
- **Identifying** the limitations associated with the current methods
- **Designing** new fabrication methods for faster throughput to overcome the practical impediments, where the fabrication process is based on conventional tools, either EBL or FIB, such that current nanofabrication users can adopt and benefit conveniently
- **Verifying** the utility of the novel fabrication method for nano-structures on master stamps through multiple replication techniques, and **validating** through selected applications in the areas of sensor and flexible electronic technologies

### 1.5. Summary of Report

The thesis report aims to provide a thorough account for the knowledge gained through the various studies related to inspiring the design of the fabrication methods, and for the techniques developed in demonstrating the feasibility and utility of the novel fast fabrication process for creating nano-structured master stamps.

Following the *Introduction to Surface Nano-Structures* (Chapter 1), where the concept of surface nano-structures is introduced through brief application examples and fundamental approaches to construction, a discussion on the *State-of-the-Art Fabrication Methods* (Chapter 2) for creating master stamps is given. In this second chapter, basic stamp and template structures are presented to assist in the discussion on the characteristics of the three conventional methods examined: FIB, EBL, and LIL. A discussion on the *Limitations of Current Fabrication Methods* (Chapter 3) follows, where
key challenges corresponding to the conventional methods are highlighted. The discussion is reinforced by results from hands-on assessments.

In the next chapters, the research advancements to new science and engineering are presented. The concept of *A Novel Method for Fast Fabrication of Master Stamps* (Chapter 4) is presented. In this forth chapter, the approach to improving the fabrication throughput and hence lowering overall fabrication costs, and the inspiration to this solution, are methodically discussed. Elements of the approach are compared and contrasted to similar techniques in other uses. The *Fabrication Process for Master Stamps* (Chapter 5) is presented next. In this fifth chapter, each step of the process flow is presented sequentially, and discussed in detail. To assess the quality of the master stamps, *Replication Techniques Using Master Stamps* (Chapter 6) are developed and employed to create large volume replications and secondary masters. The techniques and know-how learned are shared in this sixth chapter. To complete the assessment of the master stamps and process, structural analysis and fabrication yield estimates are given in the *Fabrication Results and Analysis* (Chapter 7). Further, a thorough comparative evaluation on the throughput improvement and the cost savings between conventional versus the fast fabrication process is given. Lastly, the utility of the nano-structured stamps is validated through *Exemplar Applications with Surface Nano-Structures* (Chapter 8), where integrated sensors and surface plasmon resonance based sensing using surface nano-structures are discussed.

Formal contributions to the scientific and engineering community from this research work are described in the *Contributions* (Chapter 9). The thesis report is concluded with thoughts on *Future Work* (Chapter 10) and the *Conclusions* (Chapter 11). The Appendices A to C give additional information on fabrication tools, processing chemicals, and basic fabrication processes for other polymer electronic devices used in this research.
2. State-of-the-Art Fabrication Methods

2.1. Master Stamps and Templates for Replication

Replication is one of the most effective approaches to large volume production of surface nano-structures (see Chapter 1.3 and 1.4 for discussion on the advantages of replication over other approaches). In replication, stamps or templates are inherently required as sources for the pattern to be recreated. Source structures for most replication can be categorized into two classes: i) protruding, out-of-plane structures, such as nanopillars, nano-ridges, etc.; and ii) depressed, into-plane structures, such as nanoholes, nano-wells, etc. In this report, surfaces that contain primarily protruding nano-structures are referred to as stamps, while surfaces that contain mostly depressed nano-structures are referred to as templates. Figure 2-1 shows a quartz stamp containing arrays of protruding quartz nanopillar structures.

A group of similarly arranged structures is referred to as an array. Tens of thousands of nanopillar arrays on the surface of the stamp shown in Figure 2-1 combine to form a feature region, in this case, spanning 1 cm by 1 cm.

Figure 2-2 shows two other types of structures for replication. Figure 2-2-a shows a quartz stamp, where groups of protruding pillar-like nano-structures form a bundle. At the center of the bundle is where the tallest pillars are located, while the surrounding structures taper off to diminish, following the contour of a dome. Figure 2-2-b shows a quartz template, where nanohole structures are periodically arranged to be in a square lattice (formation).
Figure 2-1: A quartz nanopillar stamp on a 1 in. by 1 in. quartz substrate containing 1 cm by 1 cm feature region. The inset shows a small section of the features with high magnification (SEM) imaging. The quartz stamp is coated with a thin layer of Cr (30 nm) to improve photography for the diffractive colouring effects displayed by the nanopillar features. This example is produced using the techniques developed in this work.

The structures shown in Figure 2-1 and Figure 2-2 can be recreated in various materials using several replication techniques. Often, master stamps or templates are created in hard and durable substrates for easier handling, compatibility with more replication techniques, and better replication reliability over larger surfaces. Because many of the process tools and methodologies in nanofabrication are derived from semiconductor processing techniques, the most common substrates are silicon and other semiconductor wafers. However, because several of the replication techniques involve lithographic procedures, quartz, sapphire, clear plastic resins, and others are also often considered.
In the following sections, conventional tools and methods for creating these nano-structures as master stamps or templates are examined.

2.2. Overview of Current Fabrication Methods for Original Masters

There are few and limited number of fundamental methods in fabricating surface nano-structures using the top-down approach. Three of the most widely employed
fundamental methods are discussed here; they include the use of: 1) the FIB; 2) the EBL; 3) and the LIL. Figure 2-3 shows examples of a FIB tool (a), and an EBL tool (b), and an optical table for LIL custom setup (c).

![a) b) c)](image)

**Figure 2-3: Examples of equipment for fabrication of original surface nano-structures: a) a focused ion beam tool; b) an electron beam lithography tool; c) an optical table for laser interference lithography custom setup.**

The FIB tool is applied to directly mill the surface of a substrate. It is a primarily subtractive process where material is sputtered away (much like the act of milling in the macro-scale) by a focused beam of ions. A key characteristic of FIB machining is that the material removal rate is largely dependent on the material sputtering yield.

The EBL tool is used to expose regions of electron beam sensitive resist typically coated on the surface of the target substrate in which the final nano-structures are to be transferred into. Electron beam resists can be either positive or negative, resulting in formation or removal of structures in the exposed region respectively. Unlike FIB machining, EBL patterning of nano-structures require post-patterning processing to realize the final nano-structures.

LIL uses the wave properties of light to create interference patterns that are in the range of nanometers. The periodic light interference pattern is focused onto light-sensitive photoresists coating the surface of the final stamp substrates. Upon exposing the resist, subsequent processing allows the resist to form nano-structures corresponding to the light pattern. LIL requires a coherent light source (e.g. a laser). LIL
interference patterns can cover a relatively large surface (e.g. larger than 1 cm$^2$) all at once; however, it is limited to periodic repeated patterns attainable by laser interference.

2.3. FIB Machining of Original Structures

FIB machining of nano-structures is a direct, physical material removal process by sputtering of atoms from the bulk substrate. A focused ion-beam is directed on the surface of the target material, where it bombards away material. The beam can be directed in a path across the surface of the target such that patterns can be created. The geometry (e.g. shape, depth, side-wall cut) can be controlled by several parameters. Figure 2-4 illustrates the concept of surface patterning using an ion-beam to create a trench-like structure.

![Figure 2-4: Conceptualization of an ion-beam removing material from a substrate surface to create a trench.](image)

The FIB patterning strategy considers several design factors. They include: the intended nano-structure geometry; the material being sputtered; and intent on course or fine polishing of the removed surfaces. To achieve the desired nano-structures, several additional FIB tool parameters must be considered, including: ion beam current, beam focus spot size, beam dwell time, and beam drive (path and order).

The FIB material sputtering rates vary depending on beam particle type, beam energy, incident angles, and material properties. For example, at 30 keV, using gallium ions (Ga+), at a normal incidence, it has been reported that gold (Au) has a sputtering
rate close to 20 atoms/ion, while silicon (Si) has a sputtering rate close to 5 atoms/ion
[41].

The FIB tool is commonly use for bulk machining of Si and ceramics in the microelectronics industry. Particularly, it is most popular in semiconductor post-fabrication analysis. The typical ablation rates of Si at the intergrated-circuit (IC) editing beam current of 10 nA, can be rather low at 2.7 µm³/s [65]. At packaging level, higher currents greater than 100 nA can be applied to achieve 30 µm³/s. Some of the latest ablation rates achieved using, for example, the new Hitachi NB5000 FIB, has been reported to reach 70 µm³/s at 40 nA, and 130 µm³/s at 61 nA [66]. These reported figures are very encouraging in anticipating the throughput of nano-structure fabrication; however, it must be noted that high-current bulk ablation of surfaces is associated with large beam spot sizes, and hence, is often un-suita ble in realizing the desired nano-structures and shapes otherwise attainable by using lower currents. There is an apparent throughput versus geometry trade-off.

The phenomenon of material redeposition and thermal deformation are also significant considerations in the use of FIB tools for surface nano-structure machining.

To develop a perspective on the throughput of using the FIB tool in producing surface nano-structures, an example is examined.

Consider a glass substrate coated with a thin film of Au (100 nm). Nanohole arrays (NHA) are to be patterned on the Au film. The nanoholes are targeted to have 100 nm diameter, 500 nm spacing (pitch), and approaching 100 nm deep. A FEI Strata 235 Dual Beam SEM/FIB tool (4D Lab Nanofabrication and Nanoimaging Facility, SFU Burnaby), is employed for the study. When the FIB tool is operated at 1000 pA beam current, assigned to 300 ns dwell time, and set to take a beam path that contains 3 passes across the designed pattern region, a 20 µm by 20 µm array can be completed in 30 s.

Now consider the same substrate, using the same tool, but instead, nanopillar arrays (NPA) are desired. The nanopillars are targeted to have 230 nm diameter, 650 nm spaced, and approaching 100 nm tall. When the FIB tool is operated at 1000 pA beam current, assigned to 350 ns dwell time, and set to take a beam path that contains
3 passes across the designed pattern region, a 42 µm by 42 µm array can be completed in 74 s.

Using the experimental data obtained, the FIB throughput on the same FIB tool can be linearly extrapolated to predict the time required to produce larger areas of nano-structures. Table 2-1 summarizes the extrapolated throughput for three simple nano-arrays: a higher quality (more circular hole shape) NHA, a lower quality NHA, and a basic NPA. It must be noted that because the FIB sputtering rate of Au is one of the highest among relevant materials, it can be anticipated that directly machining the same nano-structures onto more difficult materials such as dielectrics (e.g. glass or quartz), can require significantly longer times. It is demonstrated here that original surface nano-structures covering a relatively large area of 1 cm$^2$ can require impractically long times to create; depending on the quality and type of structure, the patterning time can range from a few days for lower quality NHAs, to several continuous weeks for higher quality NHAs. While it is understood that assessment using the FEI Strata 235, a nearly 15 year old tool technology, may not provide a justified representation of the capabilities of FIB machining, it has also been confirmed by tool industry engineers that drastic improvements by orders of magnitude cannot be expected from even the latest and greatest FIB machines.

Table 2-1: Extrapolated predictions of time required to mill 1 cm$^2$ area of three simple types nano-structures: lower quality NHAs, higher quality NHAs, and basic NPAs. The FIB tool employed for the assessment is a FEI Strata 235.

<table>
<thead>
<tr>
<th></th>
<th>NHA (faster, lower quality)</th>
<th>NHA (slower, higher quality)</th>
<th>NPA (basic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions</td>
<td>50 µm x 50 µm / 8s (50nm Au-film)</td>
<td>20 µm x 20 µm / 30s (100nm Au-film)</td>
<td>42 µm x 42 µm / 74 s (100nm Au-film)</td>
</tr>
<tr>
<td>Area Milling Rate (um$^2$/s)</td>
<td>312.5</td>
<td>13.3</td>
<td>23.8</td>
</tr>
<tr>
<td>Time Required for 1cm$^2$ (h)</td>
<td>88</td>
<td>2088</td>
<td>1167</td>
</tr>
</tbody>
</table>
2.4. EBL Patterning of Original Structures

Using the EBL to produce surface nano-structures involves patterning the desired planar (2D) nano-structures on a thin photoresist layer coated on top of the final substrate. Additional subsequent processing steps are taken to convert the planar patterns into final structures either within the resist layer, or transferred into the bulk substrate beneath. While most of the processing steps following the EBL patterning are relatively quick, the EBL patterning itself can be time consuming, much like that in FIB work.

In most cases, the electron beam sensitive photoresist is deposited on the working surface of the target substrate material (the bulk material to become a master stamp). It is also necessary to have a sufficiently conductive surface for the electron beam to focus onto; when the bulk substrate itself is not conductive, a thin metal layer (e.g. Cr or Au) is usually coated in between the resist and the substrate working surface. The 2D patterns of the nano-structures are then “drawn” by exposing a focused electron beam onto the resist layer. Modern EBL machines typically have a laser feedback controlled stage and electron beam rastering subsystem that allows patterning precision down to less than 10 nm pitch.

There are two general types of electron beam sensitive resists, both commonly polymer-based: 1) positive resists that undergo a breakdown of molecular bonding when exposed to a sufficient electron beam dose; and 2) negative resists that undergo cross-linking of its polymer chains when exposed to a sufficient electron beam dose. Figure 2-5 illustrates the EBL patterning of positive and negative resists types. In positive resists, the spot exposure of electron beam forms holes following resist development. It is usually a wet chemical process involving soaking the material within a bath and agitating to remove the exposed regions. Examples of positive resists include PMMA, ZEP-520, and UV3* [67]. In negative resists, the spot exposure of electron beam forms
pillars following resist development. For negative resist development, the developer chemical removes the un-exposed regions. Examples of negative resists include maN-2400s, COP, and NEB-22* [67].

* are chemically-amplified resists

Figure 2-5: EBL patterning of a positive or negative resist on top of a glass bulk substrate coated with thin Cr conductive layer, and the resist subsequently developed to reveal structure pattern.

There are several variations in the EBL process flow in forming the final nano-structures. Its techniques are continually a popular subject of research. One variation is where the nano-structures formed in the resist material can be used as the final structures for replication use. A few relatively new resist materials have been investigated as final structural materials. The SU8 2000.x (MicroChem Corp.) is an epoxy-based photoresist, and has been demonstrated to form suitable final nano-structures in certain replication applications [68]. The HSQ (Dow Corning) is a SiO$_2$-based inorganic resist, which has been demonstrated to form comparably strong
structures as pure SiO$_2$ (a.k.a. quartz) after appropriate post-development annealing [69].

Another variation is by transferring the nano-structure patterns from the resist layer into the underlying intermediate material layers or the bulk substrate. This is a much more common approach to retaining nano-structures in EBL processes. The 2D nano-structure patterns can be directly etched down into the layers beneath the resist to form 3D structures. Anisotropic etch techniques such as reactive-ion-etch (RIE) are effective methods [70]-[72]. However, the resist containing the 2D patterns must be sufficiently resilient as a etch mask to withstand the anisotropic etch. Common EBL polymer resists are often more susceptible to the anisotropic etching than the harder substrate beneath (e.g. Si or quartz) [73]. Figure 2-6 depicts the anisotropic etching process with a sufficiently hard etch mask.

Figure 2-6: Direct pattern transfer of nano-structures in resist layer into bulk substrate using anisotropic etch, where: 1) resist mask is patterned; 2) RIE pattern transfer into substrate.

Alternatively, an inverse pattern can be created by depositing a metal film layer on top of the entire featured surface. The background area is then removed via a process known as lift-off, retaining only the metal portion in direct contact with the substrate surface. The lift-off process is typically a technique where a sacrificial material separating the target material and the substrate is isotropically etched or dissolved away such that any portion of the target material residing on top of the sacrificial material is “carried” away during the dissolution process. In this case, the sacrificial material is the resist, while the target material is the newly deposited metal film. The retained metal pattern serves as a metal etch mask, typically much more resilient to anisotropic etching than polymer resists. Finally, the pattern is etched into the substrate using RIE to form
the desired 3D nano-structures. Figure 2-7 depicts the lift-off inverse pattern transfer process.

![Figure 2-7: Lift-off inverse pattern transfer of nano-structures.](image)

Similar to the FIB machining of nano-structures, EBL throughput considerations are important in assessing its practicality in producing large area features. In EBL, the throughput of patterning a set of designs is dependent on the:

- hardware scanning rate
- resist sensitivity ($\mu$C/cm$^2$)
- beam spot-size and shape

Further, the resist sensitivity is dependent on the:

- resist material
- layer thickness
- substrate or intermediate layer material(s)
- and beam energy (keV).

Lastly, the spot-size and shape is dependent on the selected:

- beam current (nA)
- beam aperture ($\mu$m)
- dwell time (ms)
- and as well, beam energy
To develop a further insight on the conventional processes of using the EBL tool in producing surface nano-structures, some examples are examined. Consider a glass or quartz bulk substrate. Arrays of nanoholes 200 nm in diameter, 520 nm spaced, and approaching 100 nm deep are desired. Conventional methods are described below.

When using a positive polymer resist (e.g. PMMA), a thin layer of Cr or Au (e.g. 20 nm) is additionally required on the surface of the substrate prior to applying the resist. The EBL is guided to expose the exact nanohole patterns as desired. While most anisotropic etches will likely destroy the resist layer prior to etching a sufficient amount of the hard substrate beneath, the hole pattern can be transferred into the underlying metal film layer using selective chemical etch. Note that however, most selective chemical etches are isotropic, and thus will cause an undesired undercutting or enlargement of feature sizes if unaccounted for.

When using a negative polymer resist (e.g. maN-2403), the exposed regions form pillars. A thin layer of suitable etch mask metal (e.g. 50 nm of Cr, or 80 nm of Au) can be subsequently deposited, and then the polymer resist etched away to lift-off the material on top of the pillars, retaining only the desired hole patterns. The metal film containing hole patterns is then used as an etch mask for anisotropic etching to transfer the hole structures into the substrate.

Now consider the same glass or quartz substrate. Using the EBL system, arrays of nano-pillars 200 nm in diameter, 520 nm spaced, and approaching 400 nm tall are desired.

When using a positive resist (e.g. PMMA), holes can be patterned. A thin layer of suitable etch mask metal (e.g. 50 nm of Cr) can be subsequently deposited. The resist is then lifted-off to retain Cr dots representing the top-view shape of the final pillar patterns. Anisotropic etch transfers the patterns down into the substrate, and hence forming the desired pillars in the glass or quartz bulk.

When using a negative resist, a hybrid resist can be selected (e.g. HSQ) such that hard resist pillars can be created. Using the hard resist pillars as an anisotropic etch mask, the pattern can be directly etched down into the substrate. Note that perfecting a set of process flow recipe for hard resist etch mask is difficult. Further, the resilience of
most hard resists to anisotropic etching against dielectric materials for master stamps, such as quartz, is at best at equal to the bulk substrate. That is to say, in general, a 100 nm layer of hard polymer/hybrid resist will only be able to withstand sufficient anisotropic etching to transfer 100 nm deep into the surface of the substrate.

2.5. LIL Patterning of Original Structures

The method of LIL exploits the interference patterns of light to form periodic patterns with nano-scale dimensions. Light interference requires a coherence relation between two or more sources of light. More specifically, light from different sources are able to interfere when the wavelengths and polarization are matched, and there is a phase relation. A basic concept of a two-beam LIL system [48] is depicted in Figure 2-8.

![Figure 2-8: The basic concept of a two-beam LIL system: using a single laser source that is split into two parts to create an interference pattern with nano-scale dimensions, the nano-pattern is exposed onto the photoresist on top of an antireflective coating over the target substrate.](image)

In a two-beam LIL system, two coherent laser light beams can be created from a single source through a beam-splitting setup. The resulting two beams can be expanded to have a larger beam width. The expanded beam can correspondingly cover a larger desired sample surface area when brought to overlap in creating interference patterns focused on the sample surface. The sample surface is coated with an antireflective coating (ARC) on top of which is further coated with the laser light sensitive photoresist (PR). The interference pattern forms intensity maximums and minimums dependent on the wavelength of the laser used (e.g. in the range of nanometers) which results in exposure patterns on the PR. Subsequent development of the PR removes exposed
regions (for positive resists), and thus producing retained structures corresponding to the un-exposed region, intensity minimums, of the interference pattern.

The interference intensity, $I$, in the x-direction (planar), and z-direction (into the resist), are described by Equations 2-1 to 2-3 [48].

$$I = 4I_0 \sin^2 \left( \frac{\pi x}{d} \right)$$

(2-1)

$$d_x = \frac{\lambda}{2 \sin(\theta/2)}$$

(2-2)

$$d_z = \frac{\lambda}{2n_{res} \cos(\theta/2)}$$

(2-3)

where $I_0$ is the intensity of the original matching laser beams, $x$ is the horizontal direction across the target substrate surface (see Figure 2-8), $d$ is the periodical dimension of the laser interference pattern defined by $d_x$ and $d_z$ components, $\lambda$ is the incident wavelength of the laser at angle $\theta$ apart, and $n_{res}$ is the refractive index [48].

The advantages of using LIL in nano-structure patterning are significant. Large area patterning of the substrate surface can be accomplished in a single exposure. The exposure time can be as quick as a few seconds. Compared to the lengthy patterning time required in FIB or EBL (single beam raster-scanning across a large surface), the throughput improvement and cost savings are tremendous. Further, most LIL systems are relatively more straightforward to construct compared to FIBs and EBLs, allowing for more customized under-the-hood tuning of equipment parameters. Also, LIL systems are relatively low cost compared to FIB and EBL tools.
The disadvantages of using LIL, however, can be a deterring factor in certain nano-structure applications. Primarily, LIL only allows for the same pattern across the entire target surface due to the inherent nature of interference patterns that can be generated. The pattern planar dimensions are limited to $\lambda/2$. While certain complex interference patterns can be achieved with a larger number of interference sources (more split beams or more lasers), the alignment and fine tuning or the optical components to obtain the desired interference difficult. Lastly, to create varying nano-structured arrays, a variety of different interference patterns and shadow masks are needed for every pattern change, and is simply impractical if not, impossible. Figure 2-9 shows examples of the simple periodic nano-structure arrays attainable through LIL (Figure 2-9-a), contrasted to the more complex nano-structures and assortments of bundled structures un-attainable through LIL (Figure 2-9-b).

![Figure 2-9:](image)

*Figure 2-9: Example planar nano-structure arrays: a) single periodicity rectangular arrangements are attainable through LIL patterning; b) assorted arrangements of dots forming rings, concentric rings, and variable periodicity patterns cannot be achieved through LIL patterning.*
3. Limitations of Current Fabrication Methods

3.1. Technology Challenges in Conventional Methods

The fundamental methods discussed in the last chapter for producing original surface nano-structures have independently unique attributes. They are the state-of-the-art methods for originating nano-structures, yet they each possess limitations that place certain applications out of reach.

The EBL is regarded as the industry standard for originating surface nano-structures for large surfaces (e.g. wafer-sized masks for transistors). Most of the current EBL tools are strategically optimized to pattern smaller and smaller geometries to serve the electronic density needs of the semiconductor industry. As a result of this industry demand, patterning dense arrays of structures with dimensions greater than 150 nm using the EBL is typically very time consuming. While more advanced EBL machines provide higher exposure aperture options for faster large pattern writing, the focusing and tuning of such high energy electron beam is often difficult. Some of the latest and greatest EBL machines provide features like larger spot-size patterning, shaped beam patterning, as well as larger cell projection patterning; however, these tools are quite often beyond the budget of academic research institutes, and limited to only a handful of access around the world.

The FIB is typically applied in electronic post-fabrication analysis, cross-sectioning, and to assist in SEM imaging. As such, FIB tools are typically designed with beam properties suitable for fast, but large section bulk machining, or slow, but very fine machining. More recently, small area prototyping of 2D or 3D nano-structures is becoming a more popular use of FIB [41],[42],[74], however, large area high density patterning can still be very time consuming depending on the materials targeted.
There are also inherent trade-offs between applying higher beam current for a larger spot-size versus the precision of the feature edges in both EBL and FIB patterning. For EBL and FIB tools that use Gaussian beams, a larger spot-size exposes a larger circular surface area over the same exposure time. This is particularly useful in defining circular pattern shapes for nano optical and metamaterials with dimensions in the range of 150 to 400 nm. For EBL, a larger spot-size corresponds to a higher aperture setting, while for FIB, this corresponds directly to a higher current setting. However, as previously mentioned, the larger beam is also more difficult to fine tune, resulting in poorer edge definition of the spot pattern than a smaller, more focused beam. Table 3-1 summarizes the correspondence between beam spot-size versus the quality of the feature edge for EBL and FIB tools operated under different beam conditions to illustrate the trade-off.

Table 3-1: Summary of performance for EBL/FIB pattern edge sharpness corresponding to beam spot-size settings.

<table>
<thead>
<tr>
<th>Spot-size</th>
<th>Edge Sharpness</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Aperture EBL</td>
<td>Larger</td>
</tr>
<tr>
<td>Low Aperture EBL</td>
<td>Smaller</td>
</tr>
<tr>
<td>High Current FIB</td>
<td>Larger</td>
</tr>
<tr>
<td>Low Current FIB</td>
<td>Smaller</td>
</tr>
</tbody>
</table>

The LIL is a very elegant technique in creating a large area of surface nanostructures with a single exposure [47],[48],[75]. However, the pattern types and arrangements achievable by LIL is extremely limited; namely, only patterns that can be generated through laser interference can be registered on the resist. The nano-structure patterns are limited to repeated, periodic arrays, all the same across the entire sample surface. The LIL lacks the versatility that conventional EBL and FIB can provide in terms
of pattern design, rendering many advanced nano-structure arrangements impossible. Figure 3-1 illustrates a comparison of a surface nano-structured device based on EBL or FIB patterning, versus one that is based on LIL patterning. For scanning-types of patterning tools such as EBL or FIB, multiple arrays of nano-structures with different periods, geometry, and arrangements can be created side-by-side. For flood-types of patterning tools such as the LIL, only a single continuous array with a single period and geometry can be produced.

![Figure 3-1: Conceptual comparison of nano-structures in integrated devices where (right) scanning-types of patterning tools such as EBL or FIB is employed, versus, where (left) flood-type of patterning tool such as LIL is employed [76].](image)

### 3.2. Costs of Conventional Fabrication

Although scanning-types of patterning provides versatile nano-array designs that enable more applications than the faster flood-types of patterning, its slow throughput remains a technology bottleneck. Creating large area nano-structures in bulk quartz, silicon, or metal thin films using the conventional EBL or FIB methods can be extremely costly due to the patterning tool time required.
Consider the following exemplar surface nano-structure design in a metal layer above a master stamp substrate:

- 1 cm$^2$ surface region to be fully populated with either nano-holes or nano-pillars
- Diameter of the hole or pillar structures is 200 nm
- Pitch (adjacent spacing between structures) is 520 nm
- Nanoholes are patterned on a layer of 100 nm Au (the holes are 100 nm deep)
- Nanopillars are patterned on a layer of 100 nm Au (pillars are 100 nm tall)
- Carrier substrate (stamp) is a quartz wafer

The time required to create the nano-structures described are projected (linearly) based on smaller area experimentations. Note that the exemplar nano-structures are created on Au metal film layers to give a more straightforward comparison between FIB and EBL fabrication. Table 3-2 summarizes the time required to pattern the nanohole and nanopillar arrays using conventional FIB or EBL methods (see Chapter 2.3, 2.4 for the discussion on conventional methods).

All FIB experimental work were on the FEI Strata 235 Dual Beam SEM/FIB tool (4D Lab Nanofabrication and Nanoimaging Facility, SFU Burnaby). All EBL experimental work were on the Raith ELine EBL tool (4D Lab Nanofabrication and Nanoimaging Facility, SFU Burnaby).

Table 3-2: Summary of time required to pattern 1cm$^2$ area of NHA or NPAs using conventional FIB and EBL methods: The NHAs and NPAs are 200 nm in diameter, 520 nm in periodicity, on 100 nm Au film on quartz.

<table>
<thead>
<tr>
<th>Fabrication Method</th>
<th>1cm$^2$ of NHAs</th>
<th>1cm$^2$ of NPAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIB direct milling (FEI Strata DB 235)</td>
<td>&gt; 80 hrs</td>
<td>&gt; 1000 hrs</td>
</tr>
<tr>
<td>Basic parameters: 1000 pA, dwell 300 ns</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EBL resist patterning (Raith ELine)</td>
<td>&gt; 75 hrs</td>
<td>&gt; 75 hrs</td>
</tr>
<tr>
<td>Basic parameters: 10 keV, 30 µm aperture, 0.01 pC</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To further appreciate the significance of the high cost of conventional fabrication, the tool per-hour costs for four exemplary fabrication facilities in Western North America are listed in Table 3-3. The lowest per-hour cost is available at SFU. Following the patterning tool times estimated in Table 3-2, the total usage cost based on the lowest rates available (4D Labs SFU), is summarized in Table 3-4. It is evident that the cost to pattern a 1cm$^2$ surface with the exemplar nano-arrays described is non-trivial. Several applications (see also Chapter 1.2) that require larger area designs such as that for sensors and flexible electronics, are impeded by the throughput limitation for master stamps. For researchers with smaller budgets, and device manufacturers with high business demands alike, reducing the fabrication costs through pragmatic engineering problem-solving and innovation can be extremely valuable.

Table 3-3: List of EBL and FIB charge rates for selected academic nanofabrication facilities in Western North America that offer both academic and industrial accesses.

<table>
<thead>
<tr>
<th>Facility</th>
<th>EBL Academic Rate ($)</th>
<th>EBL Industry Rate ($)</th>
<th>FIB Academic Rate ($)</th>
<th>FIB Industry Rate ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SFU 4D Labs Nanofabrication Facility (Burnaby, BC, Canada, <a href="http://www.4dlabs.ca/">www.4dlabs.ca/</a>)</td>
<td>30</td>
<td>60</td>
<td>50</td>
<td>120</td>
</tr>
<tr>
<td>UofA Nanofabrication Facility (Edmonton, AB, Canada, <a href="http://www.nanofab.ualberta.ca/">www.nanofab.ualberta.ca/</a>)</td>
<td>40</td>
<td>120</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>UCSB Nanofabrication Facility (Santa Barbara, CA, USA, <a href="http://www.nanotech.ucsb.edu/">www.nanotech.ucsb.edu/</a>)</td>
<td>180</td>
<td>540</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>Stanford Nanofabrication Facility (Palo Alto, CA, USA, snf.stanford.edu/)</td>
<td>99</td>
<td>288</td>
<td>\</td>
<td>\</td>
</tr>
</tbody>
</table>
Table 3-4: Summary of calculated costs for patterning 1cm² area of NHA or NPAs using conventional FIB and EBL methods, based on SFU 4D Labs Nanofabrication academic rates. The NHAs and NPAs are 200 nm in diameter, 520 nm in periodicity, on 100 nm Au film on quartz.

<table>
<thead>
<tr>
<th>Fabrication Method</th>
<th>Cost for 1cm² of NHAs ($)</th>
<th>Cost for 1cm² of NPAs ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIB direct milling (FEI Strata DB 235)</td>
<td>4000</td>
<td>50000</td>
</tr>
<tr>
<td>Basic parameters: 1000 pA, dwell 300 ns</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EBL resist patterning (Raith ELine)</td>
<td>2250</td>
<td>2250</td>
</tr>
<tr>
<td>Basic parameters: 10 keV, 30 µm aperture, 0.01 pC</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4. A Novel Method for Fast Fabrication of Master Stamps

4.1. Achieving Faster Fabrication

The time and cost for producing original surface nano-structures is evidently high. As the desired pattern area increases, for example, from 1 cm$^2$ to 10 cm$^2$ and so on, the cost correspondingly increases in a linear fashion, quickly becoming inhibiting for many applications. The continuous use of conventional origination tools such as the EBL and FIB for several days for only a single stamp design is also impractical in many cases. Improvements to the fabrication throughput for nano-structured master stamps, whether incremental or drastic, can contribute significantly to the community of engineers and scientists concerned with producing surface nano-structures.

To reduce the patterning time required in EBL or FIB writing, typically, only the dwell time is adjustable by the user. For both EBL and FIB tools, the dwell time is a factor of beam current and dose. When the beam current is held constant, in order to establish optimal beam focus and tuning (e.g. of stigmation, aperture alignment, etc.), reducing the required dose will consequently reduce the overall dwell time. Figure 4-1 illustrates the relationship of the EBL tool run time to its determining factors as described.
The most basic electron beam shape for EBL or ion beam shape for FIB patterning are all Gaussian beams [67]. When a Gaussian beam is focused on the surface of a target material to be patterned (e.g. photoresists for EBL, or metal surfaces for FIB), a circular exposure spot is created. Thus, the most fundamental structures that can be generated using EBL or FIB are circular. A smaller dose of the energy beam creates a smaller, shallower circular hole, while a larger dose creates a larger hole, up to the size of the beam-width. For many applications of surface nano-structures, circular hole or combinations of hole arrangements will suffice. It follows that if smaller holes can be patterned using a smaller dose during the EBL or FIB writing, marking the location of the circular pattern, and subsequent batch techniques can be employed to enlarge the holes to the desired dimensions, significant time savings can be realized.

Figure 4-2 shows the conceptual process steps in creating nanohole structures from initially smaller holes using the EBL. First, nanohole patterns across the surface of the resist-coated substrate is exposed to form small holes, and hence requiring shorter patterning time (Figure 4-2-a). Following development of the positive resist, the exposed region is removed, forming an opening to the underlying layer. Subsequently, the underlying intermediate layer is etched in a manner such that it creates a larger hole positioned exactly beneath the initial smaller hole in the resist layer registered above (Figure 4-2-b). Finally, the resist writing layer containing the initial small holes is removed to reveal the larger holes now registered in the intermediate layer beneath (Figure 4-2-c). All of the fabrication process steps excluding the EBL patterning are batch processing techniques that can be completed relatively quickly compared to the
EBL patterning time. The shortened EBL patterning time is fundamental in improving the throughput and reducing cost for creating arrays of nano-structures based on circular shapes. The same methodology can be extended to the use of the FIB tool in producing surface nano-structures (to be discussed in Chapter 5).

![Conceptual process steps in creating nanohole patterns by patterning initially smaller holes: a) small nanoholes are patterned on the resist layer; b) larger nanoholes are etched in the intermediate layer directly beneath the resist layer using selective, controlled etching; c) larger nanoholes are reveal by removing the initial resist pattern layer.](image)

The enlarged nanohole array patterns can serve as a template for many subsequent uses, one of which is for the creation of the afro-mentioned nanopillar master stamps. The fabrication of nanopillar stamps on optically transparent hard materials such as quartz is not nearly as straightforward as creating nanohole array templates. Particularly for pillars that have higher aspect ratios than 1:1, a hard metal mask is often required for anisotropic directional etching [77],[78] (also see Chapter 2.4 on EBL Patterning of Original Nano-Structures); simply defining the circular dot patterns for the nanopillars in photoresist will not suffice as an etch mask. Thus, the combined challenge of reducing initial patterning time, and designing a fabrication process for out-of-plane nanopillar master stamps, requires intricate considerations. The conventional techniques for creating nanopillar master stamps are even more time consuming than nanohole templates (see Chapter 2.3 and 2.4 for discussions on conventional fabrication for NHAs and NPAs). The process of patterning, transferring, and enlarging nanohole
patterns require accurate and controlled enlargement of the holes. The process steps that follow thereafter to transform nanoholes to nanopillars on a hard transparent stamp substrate involve defining a hard metal mask using the nanohole patterns, and then directionally etching into the substrate around the metal mask. In the next chapter, the details of the fabrication process steps are revealed and discussed, and the associated challenges examined.

4.2. Enlarged Pattern Transfer Elsewhere

The concept of transferring and enlarging patterns from one nano-structured layer to another underlying layer is seen in many examples of surface fabrication. Whether the pattern enlargement is intentional or undesired, the techniques and uses are as old as the history of microelectronics itself (examples described below). What identifies the novel fabrication method for the master nano-structures presented here from existing processes is in how the pattern transfer and enlargement are executed, the selection of uniquely compatible process layer materials, and how all the subsequent process steps combine to create the final structures. To provide a perspective of pattern enlargement elsewhere in micro and nanofabrication, a few examples are discussed below. This additional insight helps in identifying the uniqueness of the novel process presented.

In traditional microelectronics fabrication, selective etching removes the material in an underlying layer where the masking layer above does not cover [79]. Many selective etchants are liquid chemical solutions, and hence, isotropic [79]. When a material beneath a masking layer is etched using an isotropic etching method, a naturally occurring phenomenon known as undercutting can occur [79]. Undercutting is characterized by an enlargement of the pattern transferred, corresponding to when the targeted material is over-etched. The shape and extent of pattern enlargement is largely dependent on the thickness of the underlying layer and the dimensions of the masking pattern openings. Figure 4-3 shows a simple illustration of pattern transfer from a resist mask layer to an underlying target layer when undercutting occurs due to the use of isotropic etching. The shape of the undercut enlargement is classically characterized with an “inverse-arch” form. This unique shape is most noticeable when the resist mask
pattern opening is small relative to the thickness of the underlying layer. The “inverse-arch” geometry becomes more of a “vertical-cut” geometry (Figure 4-4) as the thickness of the underlying layer reduces relative to both the resist pattern opening and the lateral enlargement. Controlling the accuracy of a liquid chemical etchant can sometimes be difficult, as such, over-etching is often encountered, leading to an enlarged pattern transfer from a top layer to a subsequent layer. In some instances, the undercutting is undesirable, in other cases, it can be an applied technique to achieve fabrication tasks.

![Diagram](Patterned_resist.png)

**Figure 4-3: Example of undercutting due to isotropic etching of a material beneath the patterned resist (mask).**

The extent of the pattern enlargement in a material beneath the resist masking layer can be controlled, most fundamentally, by the amount (typically duration) of etching. Further, when the underlying layer is thin relative to the mask pattern opening and the desired lateral enlargement, the above resist layer and the underlying layer combine to form an “L-shaped” or “T-shaped” overhang structure. Figure 4-4 shows such an overhang structure consisting of a PMMA (MicroChem Corp.) resist layer above a PMGI (MicroChem Corp.) pattern transfer layer. The stacked PMMA-PMGI bilayer structure illustrated is an industry standard shape [80] in many microelectronic applications. Commercially available resists and etchants (or developers) are designed to produce relatively accurate controlled lateral enlargement. Overhang bilayer resists are often used to create a more effective lift-off structure to retain inverse metal mask patterns, or to simply form overhanging micro-mechanical structures. Unlike the novel process presented (in Chapter 4.1), the controlled undercutting enlargement of the material beneath the masking layer using two polymer resists layers does not allow the top layer to be removed such that the enlarged pattern beneath can be revealed, nor can the layer beneath be subsequently applied as a hard etching mask. However, by selecting the suitable material layers, the concept of controlled enlargement of the
pattern beneath an initial pattern layer can be applied towards saving time in the overall fabrication process of creating surface nano-structures.

Figure 4-4: Example of PMMA and PMGI bilayer stack configuration with controlled undercutting; TOP – showing a lesser lateral enlargement; BOTTOM – showing a greater lateral enlargement.

Another example of pattern enlargement in the material layer beneath a resist mask layer containing smaller patterns is in a process known as quantized patterning [81],[82]. Quantized patterning is a method dating back to the 1980s [83], which allows significantly faster creation of master masks for nano-scale photolithography.

Engineers were faced with the same challenges of lengthy pattern write-times in producing nano-scale features having dimensions too large for EBLs, yet too small for laser mask writers (e.g. 150 to 400 nm). The key applications for quantized patterning were to define transistors and other electronic components, thus rectangular pattern shapes were needed. The substrates were pre-patterned, “quantized” with Cr square tiles (e.g. 200 nm) across the effective surface. Each tile was separated from its neighbouring tile by a small distance. The pre-patterned substrates, also known as mask plate “blanks”, were then coated with a positive EBL resist layer (e.g. PMMA). Tiny holes, much smaller than the tiles, were patterned roughly at the center point of where each desired tile lies. This process was known as “tagging”. The resist was developed to create through-holes exposing a small portion of the Cr tile beneath. The tiles corresponding to the small holes above were then etched away entirely, while adjacent tiles that do not lay beneath any holes were left unaltered due to shielding of the conformal resist (resist portion that covers the tile separations). Thus, by only patterning small tiny holes corresponding to each of the tiles targeted to be removed, the EBL
patterning tool time was drastically reduced compared to if the entire shape of the tile was to be patterned.

Note that while square-shaped EBL beams are available now, the specialized systems can be far more expensive than the basic Gaussian beam EBLs, and consequently rather limited in access to large microelectronic corporations or semiconductor foundries.

Figure 4-5 illustrates the concept of quantized patterning as described. The time-saving philosophy in quantized patterning is in essence the same as the novel fast fabrication method proposed (Chapter 4.1). However, the approaches differ in that the novel fabrication method proposed does not require pre-patterning of structured tiles, making it a more straight-forward method in creating surface nano-structures. Further contrasting the quantized patterning processes, where discontinuous tiles of pre-defined geometries are set, the novel fast fabrication method does not result in gapped structures, and is able to create curved elements as a trade-off to sharp rectangular edges.

Figure 4-5: Example of quantized patterning by “tagging” small holes on the resist layer using the EBL, and then etching away the corresponding pre-defined Cr tiles beneath to create the desired final pattern.
5. Fabrication Process for Master Stamps

5.1. Overview of Process Steps

The proposed novel method for faster fabrication of original surface nano-structures creates smaller structures initially to reduce patterning tool time. In this method, nanohole patterns are created using the most basic Gaussian circular shaped beam. Based on these basic circular structures, arrays of holes and more abstract arrangements, can be derived for various applications. To obtain protruding, out-of-plane structures, such as pillars, subsequent process steps create hard etching masks to help transform the 2D nano-patterns into 3D structures. Both the planar dimensions and the height of the final protruding nano-structures can be adjusted based on design needs. The combination of small structure patterning, subsequent enlargement to obtain larger dimensions, and transforming 2D patterns into 3D structures, form the set of procedures for the proposed novel fast fabrication process. This method enables the creation of original surface nano-structures for use as master stamps or templates that cover larger surface areas than what the conventional methods can accomplish at much faster throughput and lower costs [76].

Figure 5-1 illustrates the concept of the novel fast fabrication method by contrasting the initial and final structures created through the process. A pair of nanoholes with diameter much smaller than the final intended dimension is initially patterned on the set of process material layers above the substrate (Figure 5-1-a). By the end of the fabrication process, a pair of nanopillar structures located about the center of the initial nanoholes is created. The final 3D nanopillars protrude out-out-plane, and are much larger in diameter than the initial nanohole pattern. To create initial holes of a diameter as large as the final pillar structures would require significantly longer patterning tool time (a thorough discussion on the time and cost savings is given in Chapter 7.1).
Figure 5-1: **Initial and final surface nano-structures using the fast-fabrication process:** 

- **a)** small 2D nanoholes initially patterned on the process layers;  
- **b)** large 3D (protruding out-of-plane) nanopillars following final transformation onto the hard substrate beneath.

Figure 5-2 gives examples of actual patterned structures corresponding to that illustrated in Figure 5-1. Figure 5-2-a shows the top view of exemplar small nanoholes patterned using EBL. The small nanoholes are patterned on the fabrication process layers (to be discussed in the subsequent sections). The fabrication process layers reside on top of the hard substrate (e.g. quartz) where the master stamp is to be patterned onto. The diameters of the exemplar small holes are 100 nm. Figure 5-2-b shows the top view of the large nanopillars derived from the initial small nanoholes. The nanopillars are created on the bulk hard substrate, where the pillars themselves are part of the bulk substrate. The final transformation shows nanopillars that are 450 nm in diameter. Given that the area, $A$, of a circle is,

$$A = \pi \left(\frac{d}{2}\right)^2$$

(5-1)

where $d$ is the diameter of the circular structure, it is evident that the area on the top face of the final pillars in this case is approximately 20 X that of the initial small holes. Again, to pattern a circular shape with the final large planar area using a single scanning beam would be much more costly than to pattern one that is an order of magnitude smaller.
Figure 5-2 shows an angled-side-view of the large final pillars. It is evident that the aspect ratio of the pillars are larger than 1:1. As described previously (see Chapter 2.4), to create the same pillar structures on hard substrates using conventional polymer resists would be extremely difficult due to its low resistance to most anisotropic etching techniques. Further, to directly mill-out such pillar structures using FIB tools would be even more impractical (see Chapter 2.3).

The detailed process steps of the novel fast-fabrication method proposed are illustrated in Figure 5-3. The process flow is described through a total of 9 steps: 1) Preparing the necessary pattern process layers on the substrate; 2) Writing initial small patterns on the writing-layer using EBL or FIB; 3) Transferring and enlarging patterns onto the transfer layer by selective wet etching; 4) Undercutting the lift-off layer by selective wet etching; 5) Removing the initial writing-layer; 6) Depositing the positive mask material; 7) Lifting-off the backplane material by etching away the sacrificial lift-off layer; 8) Transferring the enlarged shapes onto the bulk substrate via RIE to create final 3D structure; 9) Removing the positive etch mask.

Figure 5-3 Step 1 shows the three thin film layers prepared on top of the bulk substrate that are required for the process. The “lift-off layer” is placed in direct contact with the substrate, followed by a “pattern transfer layer”. The “writing layer” follows the pattern transfer layer and forms the top most process layer. In Figure 5-3 Step 2, small nanohole patterns are written into the writing layer using a scanning type patterning tool such as FIB or EBL. The locations of the small holes mark the centre for the eventual
final structure. In the case of writing the patterns using a FIB tool, the writing layer material is physically removed during the writing process, and hence holes are created directly. In the case of writing the patterns using an EBL tool, the writing layer material should be a positive resist, such that the region of resist exposed to electron beam energy can be removed by chemically developing the resist to arrive at hole structures. The small nanoholes reveal an opening to the pattern transfer layer. Figure 5-3 Step 3 illustrates the transfer of the initial small hole patterns on the writing layer to the pattern transfer layer beneath. Through the small hole openings, the appropriate selective wet chemical etch removes the material of the pattern transfer layer isotropically, centered about the hole opening. By controlling the amount of etching, larger hole structures can be created in the pattern transfer layer directly beneath the initial small hole. Enlarged holes of any diameter up to until adjacent holes come into contact can be achieved in this manner. The large nanoholes are thus created without requiring the same lengthy amount of time that would otherwise be needed to fully expose and pattern the entire area of the structure. The writing layer in Figure 5-3 Step 3 can be selectively removed at this point to reveal pattern transfer layer beneath, which contains nanoholes of the actual desired dimensions. These enlarged nanoholes can serve as final nanostructure for a master template. If out-of-plane protruding pillar-types of final structures are desired, the following process steps (4 to 9) utilize the enlarged hole patterns in the pattern transfer layer as an intermediate template to create the final structures in the bulk substrate.
1) Prepare pattern layers on substrate

2) EBL/FIB writing layer and subsequent development (*fast write*)

3) Selective wet etch transfer layer (*enlarge*)

4) Selective wet etch lift-off layer (*undercut*)
5) Remove writing-layer

6) Deposit positive pattern material

7) Lift-off sacrificial materials

8) RIE pattern transfer to substrate

9) Remove positive etch mask
Figure 5-3: The process steps of the novel fast fabrication method for creating original surface nano-structures as master stamps or templates. The process begins with preparing the various process layers on top of the bulk substrate (Step 1); then patterning small initial nanoholes in the writing layer (Step 2); next, selectively etching the pattern transfer layer through the openings created by the small holes, creating enlarged holes directly beneath the initial small holes (Step 3); where at this point the writing layer can be selectively removed to reveal the enlarged holes beneath, such that the pattern can be used as a master template, or; further selectively etching the lift-off layer to create an undercut (Step 4); then selectively removing the writing layer material (Step 5); and subsequently depositing a positive mask material across the entire working surface (Step 6); then selectively etching away the lift-off layer sacrificial material to remove all unwanted background material (Step 7); and finally RIE to create out-of-plane pillar structures where the cross-section shape is defined by the positive mask material conforming to the enlarged hole shape (Step 8); and removing the reminder of the positive etch mask thereafter (Step 9).

To transform the enlarged nanohole structures in the pattern transfer layer into nanopillars on the bulk substrate, the fabrication process continues with Figure 5-3 Step 4. The region of the lift-off layer material directly beneath the small hole openings of the writing layer is etched by a selective etchant. The liquid chemical etchant dissolves the material isotropically in a similar manner to the other wet etch applied to create the enlarged holes in the pattern transfer layer prior (Figure 5-3 Step 3). By controlling the amount of etching, the lift-off layer is can be etched and undercut. A suitable undercut profile is where the lift-off layer is sufficiently recessed laterally relative to the layer above. When another material is coated on top of the entire bilayer surface (see also Chapter 4.2 discussion on bilayer lift-off structures), there should be a physical separation between the new coating residing on top of the pattern layer from the coating residing inside the cavity opening. Next, Figure 5-3 Step 5 describes the removal of the initial writing layer where the small nanohole patterns are registered on. An appropriate selective etch is applied to remove the writing layer material completely so to uncover and reveal the enlarged holes in the pattern transfer layer. Figure 5-3 Step 6 shows the deposition of the positive mask pattern material covering the entire feature surface. The mask material is directionally deposited, ideally at a normal angle to the substrate plane, so to create a step separation between the mask coating residing on top of the pattern transfer layer from the mask coating residing inside the enlarged hole cavity. This mask
material must be a metal or other hard material that provides good etch selectivity against the bulk substrate beneath. The material portion in contact with the bare substrate surface inside the hole cavity is to be retained. Subsequently, Figure 5-3 Step 7 shows the positive mask pattern retained after lifting-off the unwanted backplane material. The sacrificial lift-off layer material is etched away using a selective etchant such that any backplane mask material and pattern transfer layer material residing on top of the lift-off layer are all lifted away during the process. The remaining mask material that once resided inside the enlarged hole cavity now shows an inverse of the hole patterns, shaped in circular disks. In Figure 5-3 Step 8, the positive mask pattern now serves as an etch mask for the directional, anisotropic etching of the bulk substrate material. The region beneath the circular disk patterns defined by the positive hard mask is shielded from the directional etch. Only the revealed regions are etched. The positive mask material can be selected from a list of hard materials and different thickness to influence the final geometry of the pillar structures created from the directional etch (e.g. more conical or more columnar, taller or shorter, rougher or smoother surface finishing, etc.). Figure 5-3 Step 9 shows the final pillar structures created onto the bulk hard substrate. Any remaining positive mask are removed by using the appropriate selective etchant. The out-of-plane pillar-types of nano-structures are now part of the bulk substrate of the master stamp, and can be applied towards a variety of replication techniques.

In the following sections, each of the key fabrication process steps introduced are discussed in further detail.

### 5.2. Process Layer Materials

#### 5.2.1. Bulk Substrate

The preparation of the substrate and patterning layers begins with selecting the appropriate substrate. The durability, “pattern transfer ability”, and uniformity of the substrate material are important factors in consideration. Most substrates manufactured for microelectronics applications are fine-polished at least on one side such that the surface uniformity is adequate for nano-scale patterning. Commonly available
microelectronics wafers include silicon (Si), quartz (SiO₂), sapphire (Al₂O₃), where their bulk material composition allows for reasonable pattern transfer using directional etching. Several examples of accurate pattern transfer in the micro and nano-scale have been previously demonstrated [77],[84],[85]. Of the common materials available, quartz is the more economical choice of optically transparent substrates with several selection in thicknesses for easier handling and better durability. Quartz also has higher directional etch rates compared to the other optically transparent substrates. The requirement for optical transparency is explained later in Chapter 6. Table 5-1 summarizes the hardness, strength, and fracture toughness values for some exemplary microelectronics substrates commonly available.

Table 5-1: Selected mechanical properties of commonly available microelectronics substrates [86].

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness (Mohs Scale)</th>
<th>Strength* (MPa)</th>
<th>Fracture Toughness (MPa*m m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon (Si)</td>
<td>7</td>
<td>130</td>
<td>0.95</td>
</tr>
<tr>
<td>Quartz (SiO₂)</td>
<td>7</td>
<td>104</td>
<td>0.79</td>
</tr>
<tr>
<td>Sapphire (Al₂O₃)</td>
<td>9</td>
<td>282 – 551</td>
<td>4.2 – 5.9</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.0 – 5.5</td>
<td>66</td>
<td>0.43</td>
</tr>
<tr>
<td>Pyrex, borosilicate glass</td>
<td>5.0 – 6.0</td>
<td>69</td>
<td>0.77</td>
</tr>
<tr>
<td>SiC (hot pressed)</td>
<td>9.2 – 9.5</td>
<td>230 – 825</td>
<td>4.8 – 6.1</td>
</tr>
<tr>
<td>Nickel</td>
<td>4</td>
<td>148</td>
<td>100-150</td>
</tr>
</tbody>
</table>

* Strength for metal taken as yield strength and for ceramic taken as flexural strength.

It is also possible to carry out the fabrication process, or slightly modified versions, using other substantially hard substrate materials. Hard metals such as nickel
are excellent micro and nano-replication stamp substrates [87],[88]. Polymer resins and hard plastics, such as SU-8 and acrylcs respectively, are also applicable [89],[90]. Figure 5-4, Figure 5-5, and Figure 5-6 show a Si wafer, quartz plate, and a Ni wafer respectively as suitable bulk substrates for the fast fabrication process.

*Figure 5-4: Si wafer as substrate for nano-structures.*
In this work, most of the exploration, characterization, and demonstrative samples are prepared on quartz substrates.
5.2.2. **Process Layers**

Three layers of thin film materials are required above the bulk substrate for the fast fabrication process. Directly on top of the quartz substrate is where the lift-off layer resides. The lift-off layer is a thin film material layer that can be selectively etched from the pattern transfer layer, writing layer, and substrate. The thickness of the lift-off layer must be appropriately designed to be within the range of the nano-structure dimensions; more specifically, its thickness determines its material surface exposed to the etchant during the lift-off step (Figure 5-3 Step 7). Its thickness also influences the geometry of the positive mask retained within the hole cavity during the deposition of positive mask material (Figure 5-3 Step 6). For example, a thin 50 nm gold (Au) film can be applied as the lift-off layer when chromium (Cr) is selected as the pattern transfer layer because selective etchants are commonly available for Au without removing the Cr. Polymer thin films such as poly(methyl methacrylate) (PMMA) and polymethylglutarimide (PMGI) can also be applied as the lift-off layer with Cr or several other metals as the pattern transfer layer above.

Following the lift-off layer is the pattern transfer layer. The pattern transfer layer is a thin film material layer that can be selectively etched to transfer and enlarge the small hole patterns from the writing layer above. The etching should not affect the lift-off layer, writing-layer, and substrate. The thickness of the pattern transfer layer influences the side-wall profile of the holes transferred into the pattern transfer layer when using isotropic etch. Due to the omni-directional nature of the isotropic etch, the thickness of the pattern transfer layer also dictates the minimum size of the achievable enlarged holes. Figure 5-7 illustrates a comparison of the conceptual isotropic etch profiles between two pattern transfer layers with different thicknesses. In this example, one pattern transfer layer is 1.5 X thicker than the other. Correspondingly, the resulting minimum diameter of the achievable enlarged hole in the pattern transfer layer beneath the small hole in the writing layer is 3 X rather 2 X the thickness of the pattern transfer layer. The conceptual illustration brings awareness to the influence of the thickness of the pattern transfer layer on the minimum size of the enlarged hole, while a more detailed discussion on the etching for pattern transfer and enlargement is given in a later section in this Chapter.
Figure 5-7: Conceptual comparison of the isotropic etch profile of thicker and thinner pattern transfer layers in the fast fabrication process.

An exemplar material for the pattern transfer layer is a thin 50 nm Cr layer. The Cr layer can be applied beneath a PMMA writing layer (for EBL patterning), or beneath a Au writing layer (for FIB writing). The lift-off layer materials must be selected such that the etching is compatible as previously described.

Finally, atop of the pattern transfer layer is the writing layer. In the case of using the FIB tool for writing initial small hole patterns, the writing layer material should be a material sufficiently thin, smooth, but able to provide adequate protection of the layers beneath from selective etchants in subsequent processing steps. This material can be for example, a thin 50 nm film of Au. In the case of using the EBL tool for patterning initial small holes, the writing layer material should be a positive electron beam resist sufficiently thin, smooth, but also able to provide adequate protection of the layer beneath. This material can be for example, a thin 50 nm of PMMA. Table 5-2 lists a few example combinations of process layer materials that etch compatible in the fast fabrication process.
**Table 5-2: Selected examples of compatible process layer materials for the fast fabrication process using EBL or FIB writing.**

<table>
<thead>
<tr>
<th>Writing Tool</th>
<th>Lift-off Layer</th>
<th>Pattern Transfer Layer</th>
<th>Writing Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBL</td>
<td>Au</td>
<td>Cr</td>
<td>PMMA</td>
</tr>
<tr>
<td>EBL</td>
<td>Cu</td>
<td>Au</td>
<td>PMMA</td>
</tr>
<tr>
<td>FIB</td>
<td>PS*</td>
<td>Cr</td>
<td>Au</td>
</tr>
<tr>
<td>FIB</td>
<td>Cu</td>
<td>Au</td>
<td>PMMA</td>
</tr>
</tbody>
</table>

* polystyrene

Deposition of the thin film materials can be by either physical vapour deposition (PVD) for metal materials, or spin-coating for polymer materials. Three general types of PVD are available: sputtering, electron beam evaporation deposition, and thermal evaporation deposition. Of the three common methods available, both sputtering and electron beam deposition are processes that can possibly expose underlying material surfaces to charged particles (ions or electrons). The radiation energy can undesirably damage material layers, particularly in polymers. As such, thermal deposition is primarily used in preparing most samples. An extended description of the thermal deposition tools and metals used is provided in Appendix A. The deposition of polymer materials such as EBL resists is carried out by conventional spin-coating tools. Examples of the spin-coating tools and polymers used are provided in Appendix A and Appendix B, respectively.
5.3. Pattern Writing

5.3.1. Small Hole Patterning Using EBL

Traditionally, EBL tools are better equipped with more precise sample stages and more effective pattern scanning hardware for larger wafer areas than standard FIB tools. Although a new generation of ion beam based wafer-scale patterning tool, known as ion beam lithography (IBL) [91], has very recently been introduced into the industry, these types of equipment are not yet widely available to nanofabrication facilities around the world. As such, the EBL tool is still the equipment of choice when patterning larger nanofeatured surfaces, say, of areas greater than 1 cm$^2$.

When the EBL is selected for the initial pattern writing described in Figure 5-3 Step 2, a positive EBL resist should be used as the writing layer (see Table 5-2). One of the most common positive-tone ebeam sensitive resists is PMMA. PMMA is relatively low cost compared to several other common ebeam resists. It is high resolution, high sensitivity, and has a relatively long shelf life [92].

Exposing the PMMA resist with a basic Gaussian beam creates a circular spot, known as a single dot-exposure. The exposed spot-size is controlled by the beam energy and exposure dose (see also Chapter 2.3 EBL Patterning of Original Nano-Structures and Appendix A on EBL tool example and parameters). The spot-size effectively determines the subsequent hole dimension following resist development. Since the objective in the initial writing step is to create small tiny holes just sufficient to mark the center location of each of the final larger hole structures, the dose should be minimized as much as possible while still sufficient to create a through-hole structure. Figure 5-8 illustrates a comparison between sufficient and insufficient ebeam spot exposures on a positive resist layer. In the case of insufficient ebeam exposure (Figure 5-8 LEFT), when the ebeam dose is adjusted too low, the region of the exposed resist may extend completely through the thickness of the resist. In the case when sufficient ebeam exposure is made (Figure 5-8 RIGHT), the region of the exposed resist should reach thoroughly across the thickness of the resist, such that a through-hole structure is defined. In the fast fabrication process, in order to selectively etch the pattern transfer
layer, the small initial holes in the writing layer resist must create a through-hole to reveal an opening to the surface of the material beneath (see Figure 5-3 Step 3).

![Diagram showing ebeam (insufficient exposure) and ebeam (sufficient exposure) with incomplete hole and through-hole](image)

**Figure 5-8: Conceptual comparison of ebeam spot exposure of positive resist, where in: LEFT – shows insufficient exposure leading to an incomplete hole spanning only partly the thickness of the resist layer; RIGHT – shows sufficient exposure leading to a complete through-hole spanning the entire thickness of the layer.**

To minimize the exposure dose required, the thickness of the resist can be reduced to allow faster exposure. Not only does a thinner EBL resist writing layer reduce the exposure time needed to create complete through-holes, it also reduces the amount of electron charge build-up in the resist layer (a thinner resist layer means less non-conducting material to aggregate charge) [67]. However, a sufficient layer thickness must still be maintained to protect the underlying layers from anticipated etchants in order for the pattern transfer and enlargement to be effective in subsequent process steps.

Figure 5-9 shows a series of SEM images of the surface of the EBL writing layer containing small initial hole structures. The resist layer thickness in examples shown is 50 nm. The lighter-shaded circular region are the small holes created in the resist following ebeam exposure and resist development (resist development is discussed in more detail later in this section). The exposure doses corresponding to the structures shown in each of the Figure 5-9-a through Figure 5-9-e are 0.02, 0.04, 0.08, 0.16, and 0.32 pAs respectively. The increasing doses result in increasing hole sizes, from 65 nm up to 195 nm. The EBL beam energy applied in the examples shown in Figure 5-9 is 30 kV at 30 um aperture.
All EBL patterning were carried out on the Raith ELine EBL tool (4D Lab Nanofabrication and Nanoimaging Facility, SFU Burnaby).

Figure 5-9: SEM images of nanohole structures created in the writing layer PMMA resist following exposure and development. A Raith ELine EBL is used to pattern the exemplar nanoholes, at 30 kV and 30 µm aperture. The doses are: 0.02 pAs (a); 0.04 pAs (b); 0.08 pAs (c); 0.16 pAs (d); and 0.32 pAs (e). The increasing doses correspond to the increasing hole diameters.

Figure 5-10 shows another series of SEM images of initial small nanohole structures in the writing layer. The EBL beam energy applied in this set of examples is 10 kV at 30 µm aperture.
Figure 5-10: SEM images of nanohole structures created in the writing layer PMMA resist following exposure and development. A Raith ELine EBL is used to pattern the exemplar nanoholes, at 10 kV and 30 µm aperture. The doses are: 0.006 pAs (a); 0.008 pAs (b); and 0.01 pAs (c). The increasing doses correspond to the increasing hole diameters.
The exposure doses corresponding to the structures shown in Figure 5-10-a through Figure 5-10-c are 0.006, 0.008, and 0.01 pAs respectively. As expected, the hole sizes increase with increasing dose similarly to that shown in Figure 5-9. However, it is evident that the dose required by the 10 kV ebeam to create hole structures of similar dimensions to that by the 30 kV ebeam is almost an order of magnitude lower. Clearly, to optimize the patterning time required, the 10 kV ebeam is a more effective choice over the 30 kV ebeam for the 50 nm PMMA resist. In fact, it is well known that an ebeam operated at a higher kV will typically result in a smaller exposure spot size, and also lower the sensitivity of the resist [67]. A deeper discussion on the ebeam operating voltage and energy effects on patterning will not be provided here as it is outside the scope of the thesis.

It is shown that in general, as the applied dose increases, the exposed spot size correspondingly increases to a certain limit. The resulting hole diameter after development is experimentally determined to resemble a logarithmic function of the exposure dose. Figure 5-11 plots (semi-log scale) the exposure dose versus the hole diameters after development of the resist, based on a set of dose characterization arrays containing a battery of 200 µm by 200 µm nanohole arrays. The ebeam is operated at 10 kV and 30 µm aperture. The individual nanoholes are arranged in a square lattice and spaced 520 nm apart within each 200 µm by 200 µm array. Thus, each array contains approximately 150 thousand nanoholes. Groups of the 200 µm by 200 µm arrays are assigned different exposure doses and examined under the SEM for the hole size after exposure and resist development. Notably, to create 300 nm diameter holes in the PMMA resist under the specified EBL beam conditions, approximately 0.2 pAs exposure dose is required. Contrasting to 100 nm diameter holes, approximately only 0.01 pAs is required. The dose difference required for a 300 nm hole versus a 100 nm hole is a significant 20 X difference.
Figure 5-11: EBL (Raith ELine) dot exposure dose versus resulting nanohole diameter following resist development, using EBL beam setting of 10 kV and 30 µm on 50nm PMMA writing layer.

The exposure dose is a determining factor of the dwell time, which contributes to the overall patterning time of each nanohole array arrangement (see also Chapter 2.4 and Chapter 4.1 for previous discussions on EBL patterning time factors). Recall that the other fundamental components of the EBL run time include beam settling, stage move, stage settling, and transfer times (Figure 4-1). These components are typically elements of EBL system that cannot be altered by user designs. For a given pattern area, and the same number of spot dwellings, the time required for these actions always remain the same. The only variable element is the dwell time. Figure 5-12 plots the exposure dose versus the patterning time for the same dose arrays as described earlier. For a constant set of hole pattern arrangement and array size, the patterning time is observed to increase linearly as the exposure dose increases. The 0.2 pAs exposure dose corresponding to 300 nm hole diameter in the writing layer resist is shown to require more than 2 min 30 sec to expose, while the 0.01 pAs exposure dose that corresponds to 100 nm hole diameter is shown to require close to only 30 sec. A significant patterning time difference of approximately 5 X difference is observed between patterning a 300 nm hole over a 100 nm hole. As such, it is evident that by writing smaller initial holes in the writing layer, the patterning tool time is significantly reduced, demonstrating the advantage of the “fast fabrication” process over conventional methods.
Figure 5-12: EBL (Raith ELine) dot exposure dose versus patterning time required for 200 µm by 200 µm arrays of nanoholes, arranged in square lattice and spaced 520 nm apart, using EBL beam settings of 10 kV and 30 µm on 50nm PMMA.

5.3.2. Developing EBL Resist

Following the EBL exposure, the resist must be developed in a suitable developer. Development is typically a chemical process wherein the substrate along with the exposed patterned material layer is submerged within the liquid developer solution. For the fast fabrication process, care must be taken to ensure that the developer selected is compatible with the subsequent layers and substrate layer. In most cases, a developer for a basic ebeam or photoresist is designed by the manufacturer to be compatible with metals and most microelectronic substrates. For PMMA, the basic developer is mixture of isopropyl alcohol (IPA) and methyl isobutyl ketone (MIBK). The parameters for resist layer development, such as duration, temperature, agitation, are experimentally determined based on manufacturer recommendations and resist layer conditions. The resist layer conditions may vary dependant on the amount of pre-exposure soft baking, temperature of the bake, the exposure dose, etc. The techniques and exemplar recipes for development is further given in Appendix B.
When the development or exposure, or combination thereof, of the resist layer is insufficient, or unsuitably executed, the resulting holes may not take shape as precisely designed. Previously in Figure 5-8, the effects of insufficient exposure is illustrated. Here, Figure 5-13 compares two sets of nanoholes both receiving sufficient exposure dose, but one subjected to sufficient development (Figure 5-13-a), while the other insufficient (Figure 5-13-b).

In the contrasting example, the resist layer in Figure 5-13-a was soft baked prior to exposure for only 2 min. The resist layer was developed for 90 sec with mild agitation in a MIBK:IPA developer. The holes marked by a lighter shaded rim in the SEM image show no debris inside the cavity. The resist layer in Figure 5-13-b was soft baked for 4 hrs prior to exposure. The corresponding resist layer was developed for 120 sec with the same mild agitation and MIBK:IPA developer of the same composition. The holes in Figure 5-13-b clearly show a greater amount of residual resist material inside the cavity than that in Figure 5-13-a.
Figure 5-13: SEM images of nanoholes on the surface of resist layers of two samples prepared differently, but both receiving sufficient dose: a) resist layer soft baked for 2 min prior to exposure, and developed for 90 sec; b) resist layer soft baked for 4 hrs prior to exposure, and developed for 120 sec.

The comparison presented in Figure 5-13 exemplifies the importance of applying the appropriate and adequate development recipe based on resist layer and exposure conditions. As described in the fabrication flow (Figure 5-3), a thorough hole opening in the resist layer is needed in order to access the pattern transfer layer beneath for pattern transfer and enlargement. Incomplete holes or partial blockage within the hole cavity due to inadequate resist development will result in limited etchant flow and diffusion during the pattern transfer step (Figure 5-3 Step 3), giving poor control of the etching process. The pattern transfer and enlargement will be consequently irregular and incomplete.
5.4. Pattern Transfer Layer Enlargement

Following the creation of the small holes in the writing layer (Figure 5-3 Step 2), the pattern is transferred and enlarged into the material layer beneath (Figure 5-3 Step 3). As described previously (Chapter 5.2.2), when the pattern transfer layer is a metal material, it provides the option of creating a hard template mask in the partial fast fabrication process (ending at Figure 5-3 Step 4). To transfer and enlarge the hole patterns into the metal pattern transfer layer, a wet chemical etchant is applied. The entire sample piece is placed into the etchant bath and allowed to etch for a timed duration. Etch parameters include solution concentration, bath temperature, agitation, etc. The etchant begins to dissolve away the metal material at the surface where the small initial writing layer hole creates an opening beneath. The amount of etching, primarily dictated by the duration and concentration of the bath, corresponds to the amount of lateral hole enlargement.

Figure 5-14 shows an example of a Cr pattern transfer layer hole enlargement beneath a PMMA writing layer containing small initially patterned holes. The figure shows a SEM top view of a segment of the sample with corresponding schematic of its cross-sectional view. As annotated, the initial small holes in the PMMA are approximately 100 nm in diameter while the enlarged holes in the Cr are approximately 380 nm, which is almost 4 X the enlargement. The thicknesses of the PMMA and the Cr layers are both 50 nm. The Cr wet etching process is isotropic, as such, the material is removed symmetrically in all directions (see Figure 5-7). The enlarged Cr holes are, inherently, precisely centered about the center of the small PMMA through-holes where the etchant enters.
Figure 5-14: Example of Cr pattern transfer layer hole enlargement beneath a PMMA writing layer with initial small holes.

As mentioned, the extent of the enlargement in the pattern transfer layer can be controlled. Figure 5-15 shows two SEM top view images of Cr hole enlargements beneath small PMMA holes after completing the enlargement step (Figure 5-3 Step 3) of the fast fabrication process. Figure 5-15-a shows a sample where the Cr holes are enlarged to 375 nm in diameter. Its initial small PMMA through-holes are 100 nm in diameter. Figure 5-15-b shows a sample where Cr holes are enlarged to only 200 nm diameter. Here, its initial small PMMA through-holes are also 100 nm in diameter.
Figure 5-15: SEM images (top view) of enlarged Cr holes of different sizes beneath initial small PMMA through-holes; a) Cr enlarged to 375 nm in diameter, beneath 100 nm PMMA small hole; b) Cr enlarged to only 200 nm in diameter, beneath 100 nm PMMA small hole.

The difference in enlarged diameter can be controlled by the duration of etch. A strong etchant (highly concentrated) may require only a short time to etch enlarge a grossly large hole. The difference between creating a 200 nm enlargement versus a 250 nm enlargement may be only a matter of a few seconds delay. Since the etch process is handled manually, timing errors must be anticipated and the process engineered for repeatability. The etchant can be diluted sufficiently such that the enlargement process spans a longer duration, and hence, a larger window of time is available for manual handling and removal of the sample. In this way, the enlargement can be much more
precisely controlled. Examples of Cr nanohole enlargement recipes are given in Appendix B.

By applying larger etch timing windows, a variety of enlargement sizes can be achieved, even to the extent of over-enlargement to create arrays of star-like nano-structure shapes. Figure 5-16 shows an SEM image of such star-like nano-structures as a result of over-enlarging the Cr holes to 780 nm where the initial small holes in the PMMA layer are spaced only 650 nm apart. The resulting star-like structures are also spaced 650 nm apart, and configures in a square lattice, each located in between adjacent four over-enlarged holes. Thus in summary, the upper-limit of the enlargement is bounded by the distance between two adjacent structures; in many cases, this distance is the periodic spacing between nanohole structures.

![Figure 5-16: SEM image (top view) of over-enlarged Cr holes creating star-shaped structures on Cr pattern transfer layer.](image)

In cases where the initial small through-holes are incomplete, the subsequent (see Chapter 5.3), pattern transfer layer enlargement may have poor enlargement control, or simply outright fail. Figure 5-17 shows a SEM image of a sample that has a portion of incomplete PMMA through-holes beside a portion of complete PMMA through-holes. Beneath the incomplete through-holes, the Cr pattern transfer layer material is unaffected by the Cr etchant. Whereas beneath the complete through-holes, enlarged Cr holes are created.

In this example, the portion of incomplete through-holes was created by applying a very light pressure on the PMMA material surface when heated, after the initial small
holes were created; the PMMA material surface was deformed and the small holes were sealed in the particular region.

The contrasting regions of through-holes and incomplete holes illustrate the significance of completing each prior process steps precisely and adequately such that subsequent process steps are not unfavorably inhibited.

![Figure 5-17: SEM image (top view) of a fast fabrication sample showing effects of incomplete through-hole in PMMA writing layer inhibiting Cr etch enlargement.](image)

5.5. Lift-off Layer Undercutting

The lift-off layer is included in the fabrication process to create a separation between the backplane material on top of the lift-off layer and the positive mask material subsequently deposited inside the enlarged hole cavity (Figure 5-3 Step 6). To create an undercut structure, the lift-off layer is etched by subjecting the entire sample piece in a wet chemical etching bath (Figure 5-3 Step 4). Here, the wet chemical etch process is predominantly isotropic as well. The undercut etch is in essence an enlargement etch like that in the enlargement of the hole patterns in the pattern transfer layer; however, the enlargement needs only be slightly larger than the enlarged hole in the pattern transfer layer, and does not require perfect symmetry. On the other hand, similar to the enlarged holes in the pattern transfer layer beneath the initial small holes in the writing layer, the undercut structure in the lift-off layer beneath the pattern transfer layer is inherently and necessarily centered about the initial hole pattern.
Figure 5-18 shows an example of a Au lift-off layer undercut beneath a Cr pattern transfer layer containing enlarged holes. The writing layer material is removed (Figure 5-3 Step 5) by subjecting the entire sample to a selective solvent that dissolves the writing layer PMMA completely. The figure shows a SEM top view of a segment of the sample with corresponding schematic of its cross-sectional view. As annotated, the Cr enlarged holes in the pattern transfer layer are approximately 200 nm in diameter, while the undercuts in the Au are approximately 420 nm in diameter. The thicknesses of the Cr layer is 50 nm while the Au layer is 70 nm (the significance of the thickness design will be discussed in the following section). Although the Au undercut boundary is not nearly as circular as the Cr enlarged holes, they provide adequate lateral recession from the edge of the Cr holes for the subsequent process steps. Further, similar to etching of the Cr layer, the etch parameters include solution concentration, bath temperature, agitation, etc. Diluting the Au etchant in this case greatly improves the window of time to handle the sample without jeopardizing over-etching. Appendix B provides some exemplar recipes for Au undercutting.
5.6. Positive Mask Deposition

Prior to depositing the positive mask pattern material onto the surface of the sample, the writing layer material must be completely removed (Figure 5-3 Step 5). When the writing layer material is a polymer resist, its corresponding organic solvents are typically selective and non-destructive towards the other process layers beneath. Further, reactive ion etch (RIE) using oxygen plasma can selectively target the polymer material with minimal damage to the metal process layers beneath when activated at sufficiently low energy. However, when the writing layer material is a metal, careful selection of a compatible etchant solution is crucial. Incompatible etchants can remove the pattern transfer layer and lift-off layer materials all together along with the writing layer, leaving nothing but the substrate behind. Exemplar instructions for removing a PMMA writing layer is given in Appendix B.
Once the writing layer is removed, the enlarged holes in the pattern transfer layer is revealed. The overhang structure created by previously undercutting the lift-off layer (Figure 5-3 Step 4) ensures a separation between any thin layer of material subsequently deposited on the revealed surface from the inside of the enlarged hole. At this point, a thin layer of material is ready to be deposited across the entire nano-feature surface, such that a positive mask pattern can be created (Figure 5-3 Step 6). The term “positive” here refers to the circular dot pattern that will outline the final nanopillar shapes, contrasting the “negative” nanohole pattern that is patterned first.

The thin film mask material must be directionally deposited at a normal angle to the substrate plane. The mask material should be a metal or other hard material that will later provide good etch selectivity against the bulk substrate beneath. Further, the mask material cannot be the same material as the sacrificial lift-off layer material (see Table 5-2 again for example combinations of process layer materials). In fact, the mask material must be resistant to the etchant required to removed the lift-off layer material, otherwise, all structures will be removed. As a result of this very crucial criteria, the selection of the process layer materials combination (Table 5-2) must incorporate the consideration of the final positive mask material as well at the process design stage. When the positive mask material is a metal, the deposition can be carried out using thermal or ebeam evaporation. Exemplar parameters for depositing thin metal films using thermal evaporation are given in Appendix A.

Figure 5-19 shows a SEM image of a segment of a sample at a 52° angle. This sample is coated with a Cr positive thin film layer (+Cr) across the entire nano-featured surface (Figure 5-3 Step 6). The +Cr portion that resides on top of the un-etched pattern transfer layer is considered as part of the backplane. The +Cr portion that resides inside the enlarged hole cavity is the final positive mask pattern. The +Cr portion that resides inside the hole cavity is in direct contact with the bulk substrate surface. Figure 5-20 further shows a higher magnification SEM image of a segment of the same sample with a cross-sectional cut-out made through the process layers and into the substrate using FIB. The higher magnification image reveals clear separation between the +Cr residing on the backplane from the +Cr residing inside the enlarged hole cavities. In this case, the pattern transfer layer is also a Cr material, but can be clearly distinguished from the +Cr by its interfacial boundary lines.
Figure 5-19: SEM image (tilted 52° view) of a sample after deposition of positive Cr mask thin film onto surface with enlarged nanoholes and writing layer removed.

Figure 5-20: Higher magnification SEM image (tilted 52° view) of a sample after +Cr deposition. A cross-sectional cut through the process layers and into the substrate reveals profile of the +Cr disk inside the enlarged hole cavity, and the undercut “T” shaped structure providing separation between the backplane and the +Cr inside the hole cavity.

Similar to the sample shown in Figure 5-18, the pattern transfer layer Cr is 50 nm thick, while the lift-off layer Au is 70 nm thick. The +Cr layer deposited is 40 nm. The thickness of the +Cr must be carefully selected so to not exceed the thickness of the lift-off layer such that a separation between the backplane and +Cr inside the hole cavity is
maintained. Since the final thickness of the +Cr further dictates the effectiveness of the pillar etch mask and the achievable height of the pillar, designing the thickness of the lift-off layer must consider the requirements of the final pillar etch mask early on.

The cross-sectional cut-out reveals the disk profile of the +Cr inside the enlarged hole cavity. It also further reveals more clearly that the separation between the +Cr material inside the hole cavity is sufficient from the backplane material stack. A “T” shaped structure is also seen, where the undercut Au lift-off layer forms the base, and the backplane Cr pattern transfer layer and +Cr residing on top forms the cap. A sufficient separation between the backplane and the +Cr disk further ensures that the lift-off etchant required later is able to enter through the gaps to remove the sacrificial lift-off material.

5.7. Back-plane Material Lift-off

The lift-off layer material can be selectively etched away using a suitable wet etchant (Figure 5-3 Step 7). Removing the lift-off layer material detaches the backplane material stack from the substrate. This action is consequentely termed “lifting-off” of the unwanted backplane material by removing the sacrificial lift-off layer. With the positive mask material previously deposited in place (Figure 5-3 Step 6), lifting-off the backplane material leads to a substrate surface that retains only the material inside the enlarged hole cavities that is in direct contact with the substrate surface. The resulting structures are circular disks of positive mask material arranged in the pattern outlined by the previously enlarged nanoholes.

Referring back to Table 5-2, one exemplar combination of fabrication process layers is Au, Cr, and PMMA as the lift-off layer, pattern transfer layer, and writing layer respectively. To selectively etch away the Au lift-off layer, a wet etchant that is compatible with Cr can be applied. The details of the etchant formulation is discussed further in Appendix B. Here, the custom setup for carrying out the Au lift-off etch process is described. Figure 5-21 shows an image of the etch bath setup without the etchant solution. The fabrication process sample is suspended vertically inside a sufficiently large beaker. For example, a 3 in. by 3 in. sample plate can be suitably fitted inside a
standard 800 mL beaker. The sample plate is suspended by two plastic tweezer clips help up by a stirring rod resting horizontally over top of the rim of the beaker. A Teflon-coated magnetic stirring rod is placed on the bottom of the beaker beneath the sample. The sample must be suspended high enough to avoid contact with the stirring rod once it is set in motion.

![Figure 5-21: Setup for the Au lift-off layer etch: The fabrication process sample (e.g. on quartz plate) is suspended vertically inside a large glass beaker. A magnetic stirring rod is placed beneath the sample at the bottom of the beaker, with enough clearance space to not come into contact with the sample when activated.](image)

Generally, basic lift-off etches for micro and nanofabrication processes are carried out in an open-top dish, where the sample is placed facing upwards, submerged inside the etchant solution. However, in the fast fabrication process, the mass of material to be lifted-off on the backplane stack is relatively significant. As a result, placing the sample faced-up in an etch bath will collapse the backplane stack rather than lifting it away. The custom etch bath setup holds the sample in a vertical position, avoiding collapse of the backplane stack. Figure 5-22 shows a schematic diagram of the lift-off etch process for Au lift-off layer samples. As the bath is stirred, the etchant is intended to flow gently across the surface of the vertically suspended sample. Over time, the Au lift-off material is dissolved by the etchant, where then the backplane material stack is detached and released from the substrate surface. The lift-off debris in this example consists of mostly the Cr from the pattern transfer layer and the +Cr from the positive
mask deposition. The small debris particles tends to float atop the surface of the etch bath.

Figure 5-22: Schematic of the lift-off etch process for a Au lift-off layer describing flow of etchant across surface of sample and movement direction of the lift-off material particles.

Figure 5-23 shows the complete etch setup for the Au lift-off etch. The etch bath containing the sample is placed on a magnetic stirring hot-plate. The magnetic stirring rod is activated to stir continuously for the duration of the etch until the entire sample surface is lifted cleanly. Here, the etchant is a dark reddish coloured solution. The inset of Figure 5-23 shows the surface of the etch bath where the lift-off debris floats atop. The stirring motion can be visualized based on the spiral pattern of the debris particles created. The floating nature of the lift-off debris is both a convenience and a hassle. When removing the sample from the etch bath, the large amount of floating debris tends to come into contact with the surface of the sample. The debris redeposit onto the nano-structured surface undesirably. Much of the redeposited particles cannot be rinsed away easily. However, because the lift-off debris particles naturally float atop of the Au etch bath, a majority of the debris can be removed manually using a filter sheet or sieve prior to retrieving the sample. In this manner, the Au lift-off etch can be executed cleanly, to obtain repeatable, consistently complete lift-offs of the backplane material.
5.8. RIE Out-of-Plane Final Structures

By this point of the fast fabrication process, the sample substrate should contain nanodisk-like structures on its feature surface (as shown in Figure 5-3 Step 7). The nanodisks serve as positive pattern etch masks to create the final nanopillar structures. The planar nanodisk shapes define the cross-sectional shape of the nanopillars when the substrate is etched perpendicularly with respect to the mask plane. Figure 5-24 illustrates the concept of directional etching of a substrate material using RIE, contrasted with the concept of isotropic, omnidirectional, etching of the same substrate. RIE etching removes the target material in a sharp directional fashion around a mask material. The mask material must be sufficiently hard to withstand the RIE longer than what is required to etch the full height of the final structures in the bulk substrate. Naturally, in order to create out-of-plane final structures that are taller than the hard masks, the hard mask must be a material sufficiently more etch resistant to the RIE etch ions than the substrate.
material. On the other hand, chemical solution based wet etching is typically isotropic. This means that the target material is etched equally in all directions. Generally, a larger selection of hard or soft masks can be used for isotropic wet etching without concern of mask degradation prior to achieving the desired etch depth. However, due to the nature of the isotropic material removal, the deeper the etch, the wider the lateral enlargement and undercutting occurs. As such, to create sharply defined tall nanopillars, directional RIE is much more effective than wet etching.

**Figure 5-24:** The concept of RIE directional etching (LEFT) contrasted with the concept of isotropic chemical wet etching (RIGHT) of bulk substrate material underneath mask patterns.

Specific formulations of ion gases can be applied in RIE depending on the material combinations of the target substrate of interest and the mask defining the patterns. Table 5-3 gives a list of selected substrate materials compatible with the fast fabrication process and the corresponding suitable RIE gases. Table 5-4 further gives example etch rates (in nm/min) for two different gas combinations applicable to etching quartz substrates beneath Cr hard masks.

**Table 5-3:** List of possible substrate materials for the fast fabrication process and their commonly known suitable RIE gases [71]-[73],[85],[93],[94].

<table>
<thead>
<tr>
<th>Substrate Material</th>
<th>Suitable RIE Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si wafer</td>
<td>Cl2, HBR, SF6, CF4</td>
</tr>
<tr>
<td>Fused quartz plate</td>
<td>SF6, CF4, CHF3</td>
</tr>
<tr>
<td>Sapphire wafer</td>
<td>SF6</td>
</tr>
<tr>
<td>Borosilicate glass plate</td>
<td>SF6, CF4, CHF3, Ar</td>
</tr>
</tbody>
</table>
Table 5-4: Example etch rates for fused quartz substrates and thermal evaporated Cr [73].

<table>
<thead>
<tr>
<th>RIE Gas Combination</th>
<th>Fused Quartz Plate</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF6 + O2 @ 100W, 20 mTorr</td>
<td>35 nm/min</td>
<td>&lt; 1 nm/min</td>
</tr>
<tr>
<td>CF4 + O2 @ 100W, 20 mTorr</td>
<td>41 nm/min</td>
<td>&lt; 1.3 nm/min</td>
</tr>
</tbody>
</table>

In the two example gas combinations and corresponding RIE operating conditions listed, the etch rates for the Cr are an order of magnitude lower than that for the quartz. It is evident that Cr is a suitable hard mask for quartz RIE following etch conditions similar to that described. Examples of specific RIE recipes used in the fast fabrication process is provided in Appendix A.

Figure 5-25 shows a SEM image of a segment of a nanopillar quartz stamp after the sample has been directionally etched and the remaining mask removed (Figure 5-3 Step 8,9).
Figure 5-25: SEM image (top view) showing a 60 µm by 60 µm section from a 1 in. by 1 in. quartz nanopillar stamp after RIE. The pillars on the sample are etched from 50 nm thick Cr disk patterns. This particular master stamp contains nano-structured regions spanning larger than 1 cm². It hosts a variety of pillar geometries and array arrangements all on the same substrate.

Figure 5-26 further shows higher magnification SEM images of the nanopillars located at Region1 of the sample shown in Figure 5-25. The pillars shown here are conical, standing approximately 500 nm tall, with a top diameter of approximately 100 nm and base diameter of approximately 400nm. The conical pillars demonstrate relatively sharp edges and flat sidewalls. It is evident that the conical pillars are not as columnar as would be expected from the conceptual RIE illustration given in Figure 5-24. The conical shape is a design feature that can be achieved based on the thickness of the hard mask defining the pillar and the RIE etch recipe. When the hard mask is designed sufficiently thin, but not too thin that it does not provide the required protection from the etching ion gases, the RIE parameters can be adjusted to effectively erode...
away the outer regions of the etch mask disk faster than the center regions [70]. In such way, conical pillars can be realized by tailoring the etch mask profile and RIE recipe.

**Figure 5-26: Higher magnification SEM images (tilted 45° view) of nanopillar structures located at Region1 shown in Figure 5-25, where: A) 500 nm tall conical nanopillars are arranged in square lattice; and B) even higher magnification image of a conical nanopillar with annotated dotted-outlines indicating the 3D structure of the pillar [76].**

Conical pillar shapes are particularly effective in embossing types of replication where pressure is required to embed the nanopillar structures into a softer material. Compared to perfectly columnar pillar shapes, conical pillars may provide better penetration and subsequent release. Further discussion on exemplar replication techniques and the respective stamp requirements are given in the following Chapter.

It is also noticeable that the sidewall and base-plane surfaces of the samples shown is not perfectly smooth. The finishing of the directionally etched surface is strongly influenced by the RIE gas recipe and parameters. Additional polishing of the structures can be implemented using anisotropic or isotropic etches to smooth out surface structures if desired [70]-[77], or further texture the surface. In Chapter 7, some examples of more finely polished pillars are discussed, while in Chapter 10, some future improvement considerations are given.

**Figure 5-27 shows higher magnification SEM images of the nanopillars located at Region2 of the sample shown in Figure 5-25. The pillars shown here are elongated, rather than circular. The elongated shape is created by initially patterning two nanoholes in close proximity to each other such that upon hole enlargement, the patterns fuse to**
outline an elongated “oval”. The elongated oval pillars stand approximately 500 nm tall, and are oriented diagonally along the plane, and placed in a square lattice. Figure 5-28 further shows higher magnification SEM images of the nanopillars located at Region3 of the sample in Figure 5-25. The pillars here are also elongate, stand 500 nm tall, but oriented linearly along the plane, and placed in a square lattice.
Figure 5-27: SEM images (tilted 45° view) of nanopillar structures located at Region2 of the sample in Figure 5-25, showing diagonally-oriented, elongated nanopillars, arranged in a square lattice [76].

Figure 5-28: SEM images (tilted 45° view) of nanopillar structures located at Region3 of the sample in Figure 5-25, showing linearly-oriented, elongated nanopillars, arranged in a square lattice [76].

A variety of more advanced pillar patterns and arrangements can be achieved. Clever layout of the nanohole arrangement combined with tailoring of the etch mask profile and final RIE recipe design collectively allow larger variations in final structures. Amidst the variations, the fast fabrication process remains fundamentally the same, retaining the high throughput and cost savings key to its methodology. In Chapter 7, further examples and results of fabricated templates and stamps are discussed.
6. Replication Techniques Using Masters Stamps

6.1. Replication of Nano-Structures on Polymer

6.1.1. Replication by Embossing

Embossing is one of the most fundamental methods for micro and nano replication using a stamp or template master. As previously introduced, fabrication by replication is by far the most effective class of techniques for large volume fabrication of surface nano-structures (see also Chapter 1.2). Fabrication by replication is versatile in that it can produce a set of different surface structures corresponding to every different master design. The output structures can be as complex as the master stamps themselves, and often with very high precision and throughput. Replication by embossing is a classic technique that presses a master containing surface structures into a target material. The concept is to allow the surface contour (e.g. out-of-plane pillars for stamps, or into-plane holes for templates) to transfer from a master to a target substrate, creating negative conforms. Generally, the target material must be softer than the master. In many procedures, embossing includes applying heat in addition to pressure when the master is brought into contact with the target substrate [95]-[99]. The stress on the master (heat and pressure) and ensuring penetration into the target materials are factors in determining the type of material that the master should be made of. Silicon, quartz, sapphire, glass, Ni, and alloys, are some of the masters demonstrated in micro and nano embossing [100]-[102]; however, Ni is by far much more durable and a better thermal conductor than the other materials [87],[88],[103]-[105], while quartz is compatible with a larger number of traditional micro and nano-fabrication tools and still offers superior durability over the brittle Si and provides optical transparency for UV-castings (a form of transfer patterning that combines imprinting with UV-curing of the target material [106]-[110]).
Micro and nano embossing spans several domains of applications, as such, several types of materials have been demonstrated in the past, including metals [111], polymers [98],[99],[102], and fibers [112]. For flexible electronics, embossing nano-structure on polymer substrates or polymer coated substrates is of particular interest. Some of the polymers suitable for basic embossing include polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polycarbonate (PC). Polymer substrates with thicknesses ranging from several millimetres to a few micrometers are most common.

Figure 6-1 describes a basic embossing process using a hard nanopillar stamp to create nanohole patterns on polymer substrates. In Figure 6-1 Step 1, a master stamp (e.g. quartz) is cleaned and treated with an anti-adhesion coating (e.g. tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane [61]). The details of the cleaning are provided in Appendix B. Next, in Figure 6-1 Step 2, the stamp is brought into contact with the polymer substrate and aligned based on replication requirements; often it suffices to place the stamp centered on the target substrate for single layer replications. The stamp is heated to the embossing temperature, typically just above the glass transition temperature of the polymer. In another variation, the polymer substrate is heated to an elevated temperature as well. It is crucial that the heating platen of the embossing apparatus transfers the heat evenly across all stamp and sample surfaces such that the temperature is distributed evenly. Then, in Figure 6-1 Step 3, pressure is applied, forcing the stamp into the polymer surface. Depending on the setup of the embossing apparatus, sometimes the polymer substrate is placed on top of the stamp, and pressed into the stamp rather than the stamp being driven into the polymer. Several variations of nano embossing tools exist on the market, as such it is crucial to experiment and characterize the embossing operations for each and every individual apparatus. In Step 3, the pressure is held for a duration of time depending on the substrate characteristics. In Figure 6-1 Step 4, the stamp is allowed to cool below the glass transition temperature. It is important that in both Step 3 and 4 that the entire embossing setup is kept isolated from large vibrations and the stamp in contact with the polymer is held without slippage. The nano-scale of the structures indicates that even the most minute movement translates to relatively large defects in the patterns transferred. Lastly, in Figure 6-1 Step 5, the stamp is released from the embossed polymer substrate by gradually reducing the
pressure. It is crucial here that the sample is fully cooled to a temperature range below softening of the polymer, before releasing such that no reflow occurs. Further, the moving arm(s) of the embossing apparatus must not allow lateral or axial movements any larger than that tolerable for the application.

**Figure 6-1:** Basic workflow of nano-embossing using a nanopillar hard master stamp: 1) A cleaned master stamp is coated with anti-adhesion coating; 2) The stamp is aligned with the target polymer substrate according to application requirements, and heated to an appropriate embossing temperature; 3) The stamp and polymer are brought into contact, pressure applied, and held; 4) The stamp is cooled while still held under pressure with the polymer; 5) The stamp is released from the polymer substrate to reveal stamped negative structures [113].

Figure 6-2 further shows an exemplar hot embossing apparatus. This setup contains two adjustable heat platens and a hydraulic pressure bottom plate that can be manually operated. This system does not provide fine micro alignment optics, however, is a relatively low cost system for basic embossing of micro and nano-scale surface structures.
Figure 6-1 describes embossing using a master stamp that contains protruding pillar-types of nano-structures. This basic embossing procedure is also applicable to master templates that contain structures that recess into-plane, such as nanoholes and nano-trenches, etc. However, because pattern transfer in embossing relies on indenting a primarily solid material, intuitively, one factor that influences the effectiveness of the embossing is the surface area and shape of the penetration contact. The structures on a master aimed to penetrate the target material should cover less surface area its backplane material. That is to say, a master stamp surface with pillar-types of structures will generally be more effective as an embossing stamp than a surface with hole-types of structures. The points of contact between a nanopillar stamp and an embossing target are at the tips of the pillars, while the points of contact between a nanohole template and a target is spread across the entire backplane. Further, for master stamps, the shapes of the protruding nanopillars also influence the its effectiveness in the embossing penetration and later release. It is intuitive that conical pillars are more effective than columnar pillars in penetrating flat surfaces and in subsequent releasing. In Chapter 7, a variety of nanopillar master stamps achieved particularly with conically tapered tips will be presented and discussed.
6.1.2. **Step-and-Repeat Replication**

An extension of the basic embossing replication method is stepping and repeating the embossing procedure across the surface of a large sheet in such way so that a larger area of surface nano-structures can be assembled [115],[116]. Similar to basic embossing in a two-plated press apparatus, step-and-repeat embossing can be designed to accept a variety of sheet substrates, including metals and polymers. Step-and-repeat is also often used to create a larger version of a master stamp that contains several rows of the same pattern designs. This larger secondary master is sometimes also termed as the “recombined master”.

Figure 6-3 illustrates the use of nano-structured stamps in step-and-repeat embossing to produce a larger area of surface nano-structures. The basic procedure takes a single master stamp and presses it into the target substrate similarly to that described in Figure 6-1. The master stamp is removed from the target substrate and brought to a next location and pressed into the target substrate at the new location. The process is iterated until the target substrate surface is patterned with the desired number of repetitions at the desired number of locations. There are several extensions to the basic step-and-repeat technique. For example, a number of different master stamps can be used to pattern a single large target sheet at various different locations by replacing a different master at each desired location. Or, multiple master stamps can be assembled side-by-side onto a single tool holder on the step-and-repeat apparatus such that each embossing cycle on a single position contains the combined pattern.
Figure 6-3: Concept of step-and-repeat embossing of nano-structures on a large sheet substrate.

In modern equipment for step-and-repeat embossing, computer guided movement can often guarantee 10, 5, or even submicron planar x-y precision. In some cases, step-and-repeat systems utilise UV-casting in place of direct embossing. UV-casting requires a UV-sensitive resist coating on the surface of a target sheet substrate. The master stamp is brought into contact and pressed into the resist layer where then UV light is exposed upon the stamped region. Usually, the master stamp or the target substrate must be optically transparent such that UV light can transmit through. Often, UV-casting provides higher precision structure conform and step-and-repeat alignment precision than direct embossing because the UV-casting process requires lower pressure contact and low to no additional heating, so the target material is less prone to undesired deformation or heat fatigue. Step-and-repeat nano-imprint lithography (NIL) is a type of technique based on UV-casting that allows nano-scale accurate stitching of patterns between each step. This type of accuracy further enables applications such as large area photonic waveguides, advanced displays, among others.

6.1.3. Roll-to-Roll Replication

Roll-to-roll (R2R) based replication has the highest throughput by far among all fabrication methods for surface nano-structures. The concept of R2R fabrication is in essence like that of magazine printing, where a roll of target sheet substrate is passed through a patterning process at a high speed to produce, for example, several hundreds of meters of completed product within hours. Some examples of R2R replication include R2R embossing and R2R UV-casting [48],[112],[117],[118].
Figure 6-4 illustrates the use of secondary nano-structured stamps mounted on a direct embossing roller assembly to produce large volume nano-structures in a R2R process. Here the secondary master stamp depicted could be a thin Ni replica of an original quartz master. A sufficiently thin Ni stamp can be bent and fitted around an embossing drum (or roller) where its non-featured side is in contact with the drum, while its nano-structured side is facing the target sheet substrate [48]. The embossing drum rotates at a specific set rate as the sheet substrate is passed through the embossing point-of-contact at a matching speed. In cases when cold embossing is implemented, no additional heat is subjected on neither the stamp or substrate. In R2R hot embossing, the Ni stamp and or the substrate may be heated, particularly, the sheet substrate may be rapidly heated at the point-of-contact using IR based heating to temporarily soften the material.

![Figure 6-4: Concept of roll-to-roll direct embossing of nano-structures on soft sheet substrate.](image)

6.2. Creation of Secondary Master by Electroforming

6.2.1. The Process of Electroforming on a Mould

Electroforming is a classic additive technique in microfabrication. It is particularly useful in creating metal structures from polymer moulds. Many lithography based fabrication processes such as photolithography and electron beam lithography creates
initial structures in polymer resist materials. These “soft” micro or nano-structures are not suitable for embossing on metal materials that are much harder than its polymer self. Instead, the desired metal can be electrodeposited onto the mould, and gradually additionally formed to a thicker bulk. Electroforming can achieve deposition rates orders of magnitudes higher than metal evaporative deposition (e.g. thermal, ebeam, sputtering, etc.). However, the electroforming process involves wet chemistry bath that brings added complexity to the overall fabrication process in considering material compatibility.

As previously described in R2R embossing (see Chapter 6.1.3), Ni secondary recombined masters can be made thin and is sufficiently durable to wrap around a R2R embossing drum. In fact, Ni is often one of the most commonly suitable metal material used in high volume micro and nano embossing, due to its suitable mechanical characteristics, well established electroforming techniques, and relatively low cost of production. In some of the most extreme cases of stamping applications, such as hard embossing on silver coins, it has been demonstrated that a Ni stamp of 150 µm thickness can be created with appropriate mechanical properties to withstand an embossing pressure of 1500 MPa at room temperature [119]. Further, for high volume hot embossing, Ni stamps are expected to withstand several tens of thousands of repetitions with cyclic heating up to glass transition temperatures of the target polymer materials (e.g. 180 °C for PMMA and 150 °C for PC).

A general process for creating secondary master stamps by creating a negative mould and then subsequently electroforming to obtain a metal replica is outlined in Figure 6-5 and Figure 6-6. The replication process can be separated into two segments: First, the creation of a negative mould on a polymer substrate (Figure 6-5); Second, the creation of the secondary positive master stamp from the negative mould by electroforming on top of the polymer template (Figure 6-6).

Creation of the negative mould by hot embossing follows that described in Figure 6-1 for basic one-to-one replications, and Figure 6-3 for recombined larger negative moulds. Once the negative mould is created, a seed layer of conformal, thin, conductive metal is coated over the entire surface of the polymer negative mould. The seed layer should provide sufficient conductivity to enable subsequent electroforming, while not
altering the mechanical structure of the replica undesirably. The seed layer should also be of material(s) that promotes good surface wetting, while not subjecting to corrosion or chemical reaction to electroforming bath. Upon completion of electroforming, the polymer negative mould is released either through mechanical delamination, or chemical dissolution of the mould (by sacrificing the mould). The replicated Ni secondary master stamp may retain a residual film layer of seed material depending on the process of release. In any case, the seed material can be removed by selective chemical etch if it is not of the same metal element, or retained as part of the structural component on the secondary stamp. Figure 6-5 and Figure 6-6 describes the two segments of the electroforming process from a negative mould as described above.

*Figure 6-5: First segment of the secondary master forming process where a negative mould is created from the original master stamp: shows process steps for creating a negative mould beginning with aligning the stamp to the polymer target substrate, then embossing the substrate, and finally releasing to reveal the negative conform.*
Figure 6-6: Second segment of the secondary master forming process where a metal stamp (e.g. Ni) is created from the polymer mould: shows process steps for electroforming, beginning with conformal sputtering a seed layer metal across the surface of the polymer negative mould, followed by electroformation of the metal bulk, and finally the sample is released.

### 6.2.2. Nickel Electroforming

Ni electroforming, like all other, consists of applying an electric potential between two conductive electrodes that are immersed in an electrolyte containing an ionic specie to be coated on one of the electrodes. When electroforming a to create a bulk stamp, the thickness of material deposited is in the micron-scale. The amount of material required to form such a bulk thickness suggests that a sacrificial electrode of the same metal specie is needed. The metal sacrificial electrode dissolves upon the application of anodic current, forming the ions that are eventually transported through the bath and deposited onto the sample connected to the cathode. The mechanical and transport properties of the deposited metal layer is a factor of several parameters, including: the bath pH, temperature, ionic conductivity of the solution, surfactant composition, current rate, cation concentration, contaminants, and stability and waveform of the applied potential.

Two common electrolytes used in Ni electroforming are the Watts and Sulfamate solutions. Considering that the Ni stamp is to be subjected to repeated thermal cycling
and pressure in R2R or other types of high volume replication processes, residual stress in the formed Ni should be minimized to help reduce the onset of fatigue cracking during use. The residual tensile stress of a Ni piece formed from a Watt bath is approximately 4 to 11 fold of the Sulfamate ones [120]. The residual stress can also be reduced by including stress reducing agents in the Sulfamate bath [120],[121]. Further, the Sulfamate-based solution is known for its high rate of deposition, and has an excellent throwing power (the ability of an electroplating solution to deposit metal uniformly on an irregularly shaped cathode) [120]. Control of the bath composition is a key element to achieving high purity, thickness, and uniformity of the stamp replica. The composition of the Sulfamate bath is provided in Appendix B.

A basic direct-current (DC) based electroforming process often suffices in replication even at the nano-scale [87],[88],[103],[105]. Pulsed alternating-current electroforming processes can provide finer grain, more uniform, and lower stress depositions, however, it’s deposition rate is often several folds slower than DC electroforming [122][123].

As described in Figure 6-6, electroforming takes place on a conductive surface onto which the intended metal forms. Thus prior to electroforming, a conformal thin metal seed layer must be deposited over the desired surface region on the mould. For example, a thin Ni metal seed layer can sputtered onto the featured-surface of the negative mould to create a conformal coating layer. Further details of the Ni sputtering is provided in Appendix A. Following the conformal Ni then film coating, the negative moulds are seeded and ready for electroforming.

Figure 6-7 gives an example of how a negative polymer mould coated with Ni seed layer is attached on a electroplating holder (4D Lab Nanofabrication and Nanoimaging Facility, SFU Burnaby). The negative mould sample should be placed nano-feature-side-up. The Ni seed layer metal should be in contact with the spring-pressure sample clips. It is best to have multiple clips holding the sample flat against the holder, close to the outer edges of the sample. The stronger the contact, the more effective the clips help maintain the polymer sample flat. Ideally a ring-like structure should be constructed to hold the sample flat against the holder while providing a very uniform electric field distribution during the electroplating process across the seeded-
surface (to avoid non-uniform growth). Further, irregular shaped seeded-surfaces, elongated seeded-surfaces, and seeded-surfaces that bleed off the edges of the samples will contribute to undesirable surface tension as the electroformation thickens, causing the Ni-formed secondary master stamps to curl (concavity).

![Image of polymer mould sample setup](image)

**Figure 6-7: Setup of a polymer mould sample on a sample holder for Ni electroforming.**

The deposition recipe can contain multiple steps of gradually increasing potentials, or only a couple rate steps. One example is to begin at a low deposition rate, closely matching the seed-layer metal sputtering rate, then gradually ramping up to a higher rate [105]. The gradually increasing growth ensures finer grains and adequate filling of nano-structure cavities with lower stress prior to more aggressive higher-surface-tension formation. Alternatively, a slightly more straightforward, yet also effective, two-step recipe [87], based on industry practice is also suitable for nano-replication. Here, a lower-rate step is first expected to deposit finer grains to fill the nano-structure cavities thoroughly, up to a thickness that exceeds the depth of the nano-structures. Then, a higher-rate step is expected to add bulk volume to the Ni-formed to create sufficient thickness for structural mechanical integrity.

Figure 6-8 shows an example of three negative mould pieces on a sample holder prior to starting the deposition in a Sulfamate bath using a gradually increasing growth rate approach. Figure 6-9 shows the samples after the first 11 µm is formed. Figure 6-10 shows the samples after a total of 236 µm is formed. Examination of the nano-structures on the electroformed Ni secondary master is given in Chapter 8.
Figure 6-8: Ni electroforming on various substrates coated with different seeding layers prior to any Ni forming: a quartz substrate is coated with Cu seeding layer; a PET substrate is coated with Ni seeding layer; another PET substrate is coated with Cr/Ni seeding layer.

Figure 6-9: Ni electroforming on various substrates after 11 µm is formed in a Sulfamate bath.
Figure 6-10: Ni electroforming on various substrates after 236 µm is formed in a Sulfamate bath.
7. Fabrication Results and Analysis

7.1. Master Structures Fabricated

7.1.1. Hole-Type Template Structures

Nanohole based templates can be created on hard substrates using only the first few steps of the fast fabrication process. As outlined in the process steps in Figure 5-3, by Step 3, enlarged nanohole arrays are created in the pattern transfer layer. At this point, the process can carry on using the enlarged nanohole patterns in the pattern transfer layer as a template to create the final pillar stamp structures, or the template can be applied in other replication procedures. In either case, enlarged nanohole array patterns created using the fast fabrication process require significantly less time and cost than conventional EBL and FIB methods. Analysis on its time and cost savings are given in the last section of this Chapter. In addition to the higher throughput, the fast fabrication process is able to yield both into-plane hole-types of structures (templates) and out-of-plane pillar-types of structures (stamps). Figure 7-1 shows a SEM image of the most basic nanohole array from a fabricated template.
Figure 7-1: SEM image (top view) of a segment from a nanohole array template containing basic circular nanoholes arranged in square lattice spaced 520 nm apart. The false colouring on the pattern transfer layer metal (Cr) helps distinguish the backplane elevated regions from the hole cavities showing the base substrate (quartz) which are uncoloured and darkly shaded.

The basic nanohole array template contains enlarged circular nanoholes patterned in the pattern transfer layer on a quartz substrate. The lift-off layer is also etched sufficiently to reveal the quartz substrate on the base of the hole cavity. The writing layer is further removed to reveal the enlarged hole patterns. The pattern transfer layer in this fabricated template is Cr. The Cr pattern transfer layer is false coloured in the SEM image to emphasize and help distinguish the elevated regions of the template surface from the indented hole cavities, which are left uncoloured, and darkly shaded. The basic circular nanoholes shown in Figure 7-1 have an enlarged diameter of 400 nm, and are arranged in a square lattice spaced 520 nm apart between each adjacent hole.

Figure 7-2 shows a SEM image of another basic nanohole array from the same fabricated template. The enlarged circular nanoholes in the Cr pattern transfer here are also 400 nm in diameter. The nanoholes are arranged in a hexagonal lattice spaced where each hole is spaced 450 nm apart from the adjacent holes.
Figure 7-2: SEM image (top view) of a segment from a nanohole array template containing basic circular nanholes arranged in hexagonal lattice spaced 450 nm apart. The false colouring on the pattern transfer layer metal (Cr) helps distinguish the backplane elevated regions from the hole cavities showing the base substrate (quartz) which are uncoloured and darkly shaded.

Figure 7-3 and Figure 7-4 show SEM images of more advanced nanohole array patterns also from the same fabricated template. In Figure 7-3, the “elongated” nanoholes are created by lining up three initial small nanoholes 100 nm apart such that upon pattern transfer and enlargement onto the Cr layer, an elongated hole shape is formed. The elongated nanoholes are diagonally oriented at 45° from the normal planar x-y axis. The holes are also arranged in a square lattice with etch structure spaced 650 nm apart from the adjacent.
Figure 7-3: SEM image (top view) of a segment from a nanohole array template containing elongated nanoholes arranged in square lattice spaced 650 nm apart. The false colouring on the pattern transfer layer metal (Cr) helps distinguish the backplane elevated regions from the hole cavities showing the base substrate (quartz) which are uncoloured and darkly shaded.
Figure 7-4: SEM image (top view) of a segment from a nanohole array template containing “L” shaped nanholes arranged in square lattice spaced 650 nm apart. The false colouring on the pattern transfer layer metal (Cr) helps distinguish the backplane elevated regions from the hole cavities showing the base substrate (quartz) which are uncoloured and darkly shaded.

Figure 7-4 shows “L” shaped nanholes created by placing three initial small nanholes perpendicularly to each other; where one marks the origin, another is offset in the x-axis by 150 nm, yet another is offset in the y-axis by 150 nm. Upon pattern transfer and enlargement onto the Cr layer, the “L” shaped nanhole is formed. As with all other basic arrangements, the “L” shaped holes in Figure 7-4 are placed in a square lattice, spaced 650 nm from each adjacent structure. The more advanced nanohole structures shown in Figure 7-3 and Figure 7-4 may provide unusually interesting optical metamaterial characteristics in various end applications, while still benefiting from the patterning time savings of using the enlargement technique in the fast fabrication process.

Figure 7-5 through Figure 7-7 show three segments from another nanohole template containing abstract patterns. These abstract patterns are created by overlapping two arrays of circular nanoholes that are arranged in basic lattices. In Figure 7-5, two sets of nanhole arrays both arrange in hexagonal lattice are overlapped and rotationally offset by 45° during initial small hole patterning. The SEM image show the template pattern after hole enlargement on the Cr pattern transfer layer. In Figure 7-6, the two sets of overlapping nanohole arrays are each arranged in square lattice. The
rotational offset during the initial patterning design is also 45°. It is clearly evident that the patterns created by overlapping arrays at 45° rotational offset are rather different in Figure 7-5 and Figure 7-6, due to the difference in their basic lattice.

Figure 7-5: SEM image (top view) of a segment from a nanohole template containing abstract patterns where two arrays of circular nanoholes both arranged in hexagonal lattice are overlapped with a rotational offset of 45°. The false colouring on the pattern transfer layer metal (Cr) helps distinguish the backplane elevated regions from the hole cavities showing the base substrate (quartz) which are uncoloured and darkly shaded.
Figure 7-6: SEM image (top view) of a segment from a nanohole template containing abstract patterns where two arrays of circular nanoholes both arranged in square lattice are overlapped with a rotational offset of 45°. The false colouring on the pattern transfer layer metal (Cr) helps distinguish the backplane elevated regions from the hole cavities showing the base substrate (quartz) which are uncoloured and darkly shaded.

Figure 7-7 shows yet another different abstract pattern created by overlapping two sets of nanohole arrays. Here, the rotational offset is 30°. The individual basic nanohole arrays are arranged in hexagonal lattice. The variety of abstract patterns demonstrated, along with both simple and advanced hole structures, combine to provide a largely versatile selection of nanohole array templates.
7.1.2. Protruding Pillar-Type Stamps

The final output of the fast fabrication process creates nanopillars on bulk hard substrates. Because the nanopillars protrude out-of-plane, the processed plates or wafers containing these structures are termed as stamps (see also Chap 2.1). As mentioned previously (see Chapter 5.8), the nanopillars created through the fast fabrication process can be either more columnar or more conical. They can also be non-cylindrical, like that shown in Figure 5-27 and Figure 5-28. Conical pillars are particularly effective in embossing techniques due to their pin-point or narrowed tips. A variety of cylindrical pillars are demonstrated using the fast fabrications process. Figure 7-8 through Figure 7-11 each shows an example of a set of uniquely shaped conical pillars.

In Figure 7-8, relatively wide conical pillars with a blunt flat top is shown. The pillars are etched in quartz substrate, and stand approximately 500 nm tall, with a top diameter of 250 nm and a base diameter of 450 nm. The pillars have highly sloped sidewalls, forming approximately 70° from the base.
Figure 7-8: SEM image (tilted 45° view) of a segment from a nanopillar quartz stamp showing blunt-top conical nanopillars created using the fast fabrication process. The image is false coloured to improve contrast to help identify the elevated and recessed regions of the surface.

The sloped sidewalls giving the pillars the conical shape is achieved by carrying out the RIE directional etch at a slightly higher reactor chamber pressure than what would provide highly vertical sidewalls, combined with a small amount of etch mask edge erosion [70]. The large blunt flat tops are achieved by designing large enlarged nanoholes that define large disk etch masks.

Figure 7-9 shows a set of small conical pillars. These pillars are approximately 250 nm tall, with the top vertex quite rounded and smoothed, and a base diameter of also 250 nm. The small conical pillars are achieved by carrying out an extended duration of RIE (the same formula as that for the structures in Figure 7-8) until the disk-shaped etch masks are almost completely eroded away from its edges inwards. The initial diameter of the disk-shaped etch masks are approximately 200 nm.
Figure 7-9: SEM image (tilted 45° view) of a segment from a nanopillar quartz stamp showing small conical nanopillars created using the fast fabrication process. The image is false coloured to improve contrast to help identify the elevated and recessed regions of the surface.

Figure 7-10 next shows a set of larger conical pillars with sharp-tips. The slope of the sidewalls is lower than that of the pillars shown in Figure 7-8 and Figure 7-9, estimated to be approximately 55° from the base. The sharp-tipped conical pillars are achieved by carrying out similar extended duration of RIE as that for the pillars in Figure 7-9, however, its disk-shaped masks are designed to be thinner such that the edge erosion can take effect more drastically with respect to the depth of the directional etch. In essence, as the quartz substrate is etched, the disk mask diameter reduces over time until it is completely depleted; in such way, a sloped sidewall is created and a sharp apex is achieved.
Figure 7-10: SEM image (tilted 45° view) of a segment from a nanopillar quartz stamp showing sharp-tipped conical nanopillars created using the fast fabrication process. The image is false coloured to improve contrast to help identify the elevated and recessed regions of the surface.

Lastly, in Figure 7-11, tall, slender, tapered conical pillars are demonstrated. To achieve these taller pillars with higher aspect ratios, a slightly thicker metal disk mask is needed. The highly vertical sidewalls is an effect of reducing the RIE reactor pressure such that the etch gas species can flow into the trenches between the pillars more effectively during the process of etching. These pillars stand approximately 500 nm tall, and have base diameter of 200 nm.
The resulting aspect ratio of the pillars shown in Figure 7-11 is approximately 2.5:1.

It should be noted here that despite the multiple fabrication steps, the nano-structure yield at the end of the full fabrication flow is excellent. It is inevitable that as a fabrication process flow becomes more elaborate, there is a higher chance of failure or errors during the execution of the various steps. Further, the more pieces of fabrication equipment is required, the higher the chances of facing equipment failure, or the more cumbersome in dealing with equipment scheduling and availability. This is a common and unavoidable fact of multi-step fabrication. However, when each of the process steps are executed without errors, the nano-structure yield on the master stamps is estimated to be greater than 99% [76].

7.2. Replicated Structures

7.2.1. Embossed Polymer Nano-Structures

The effectiveness of several fabricated master stamps are assessed by applying them in a number replication processes previously described (Chapter 6). By inspecting the replicated samples macroscopically for completeness and microscopically for
structural transfer accuracy, an informative conclusion can be made on whether the hard stamps created using the fast fabrication process provide comparable replication performance to those created using conventional methods.

Figure 7-12 shows a small piece of PC plastic plate that is embossed with a region of nanohole array patterns of one of its surfaces. The embossing procedure follows that illustrated in Figure 6-1 (see Chapter 6.1.1). The PC plate shown is approximately 3 cm by 3 cm by 2 mm, while the nanopillar hard stamp is approximately 2 cm by 2 cm. A smaller region inside the embossed area surrounding the nanohole array features is coated with a thin metal film for optical applications. Macroscopic inspection of the pattern transfer in this example shows excellent yield. The hard stamps can be reused in the embossing procedure for several cycles without any concern of nano-structure damages. Other materials tested include PS, PP, and various forms of PET, at various substrate thicknesses ranging from less than 0.25 mm to 3 mm.

Figure 7-12: Sample of a clear PC plastic plate (approx. 3 cm by 3 cm by 2 mm), embossed with nanohole array patterns on one surface using a 2 cm by 2 cm nanopillar hard stamp. The region around the embossed nanoholes is coated with a metal coating for optical applications.

Figure 7-13 shows two pieces of exemplar PET polymer sheets containing large regions of replicated nanohole arrays. The high-grade PET sheets are casted onto original quartz master stamps created using the fast fabrication process. The castings are made from quartz stamps 3 in. by 3 in. large. The two pieces shown are trimmed segments from the full castings. The PET casted sheets are thin, light-weight, and
flexible. Prior to metal deposition on the nano-feature side the PET sheets are clear, and optically transparent. A thin film of Al is coated on the nano-feature side for optical applications. To demonstrate the consistency and quality of replication across a large surface, Figure 7-14 further shows SEM high magnification images of the nanohole arrays from selected regions across the surface of the replicated plastic samples. Four regions labeled ‘a’, ‘b’, ‘c’, and ‘d’ are marked in Figure 7-13. These regions correspond to parts a), b), c), and d) in Figure 7-14. The SEM images in Figure 7-14 show consistently similar nanohole arrays in all four randomly sampled regions, where no major defects to the nanohole structures are observed. The nanohole arrays are arranged in squared lattice, and have different periodicities according to the stamp design; 450, 520, 650, and 625 nm corresponding to parts a), b), c), and d) in Figure 7-14.

Figure 7-13: Samples of large area nanohole arrays replicated on high-grade PET from quartz nanopillar master stamps. The samples are compared to a Canadian two-dollar coin. The PET surface side containing nanoholes are then coated with Al for optical applications [76].
The evaluation of the master stamps is further extended by creating recombined secondary masters in Ni and applying them in R2R large volume replication trials. The secondary Ni master stamps are produced by first creating a recombined large negative polymer mould containing patterns from several original quartz masters (Figure 6-3), then electroforming (Figure 6-6) to grow a thin, bendable, yet extremely durable master stamp sheet. Figure 7-15 shows two examples of R2R embossed nanohole array patterns on thin PET sheets. The patterned PET samples shown are segments from a large 2000 ft roll produced at 100 ft/min by an industrial partner* specializing in R2R micro and nano-patterning on plastics for optical applications. Figure 7-16 further shows a close-up view of a segment of the R2R nano-embossed PET sheet. The embossed PET sheet is 25 µm thick. The samples are held onto a thicker PET sheet for easier handling during post producing analysis. The inset of Figure 7-16 shows a high magnification SEM image of the nanoholes created on the surface of the PET. Although it is evident that some small clumps of polymer debris remain on the surface, the hole structures created are relatively circular and complete. The practicality and utility of the master stamps created using the fast fabrication process is thus verified qualitatively through both basic replication techniques, and extended, industrial high volume replication trials.
* Commercial partner outside of SFU research facilities.

Figure 7-15: Examples of roll-to-roll embossed nanohole arrays on thin PET sheets (25 µm thick) from a large 2000 ft production run [76].
Figure 7-16: A segment of a thin PET sheet from the same R2R production samples as that shown in Figure 7-15 displaying closer view of the embossed nanohole feature regions. The thin PET sheet containing embossed nanohole structure are held on a thicker PET sheet for better handling during post fabrication analysis. The inset shows an SEM image (top view) of the embossed nanohole surface found at the indicated region [76].

7.2.2. Ni Electroformed Secondary Masters

Ni electroformed secondary master stamps can be more durable and effective than the original master stamps for certain replication processes. As previously described (Chapter 6.2 and Chapter 7.2.1), creating a secondary master from an original master stamp requires first producing a negative conform of the master stamp on an intermediate substrate (e.g. on a polymer by embossing or casting), then forming a positive secondary stamp from the negative mould (e.g. by electroforming a Ni bulk).

Figure 7-17 shows an SEM image of the nanopillar surface from a segment of a secondary Ni master stamp. The Ni stamp is electroformed on a negative mould created by embossing with an original quartz stamp. The replicated nanopillars show the same tall, slender, and steep sidewalls as that in the original quartz stamp. The conical pillars stand 600 nm tall, and have a base diameter of approximately 300 nm. The electroformed Ni secondary master is 110 µm thick; the thickness is designed to be sufficiently durable to withstand vigorous handling and high number of polymer
replication cycles, but adequately thin be mounted on a R2R embossing drum. The nano-structure replication yield for the secondary master is assessed to be greater than 95%, wherein a missing or broken pillar is considered a failure.

![SEM image of Ni electroformed secondary master stamp](image)

\textit{Figure 7-17: SEM image (tilted 45° view) of a segment of a Ni electroformed secondary master stamp showing tall, slim, conical shaped pillars.}

Demonstrating excellent transfer even after two stages of recreations, first a negative mould, then a positive secondary replica, strengthens the verification that the original master stamps are suitable for multi-stage replications. Equally important, demonstrating the successful replication of Ni secondary masters from quartz original masters increases the options for stamping tools and high volume nano-structure replication techniques available in prototyping nano-structure arrays on flexible polymer substrates.

\section*{7.3. Quantitative Circularity Analysis}

It is naturally difficult to provide quantitative measure of the “quality” of the nano-structures produced. Often, quantitative measurements are based on the performance of the unique metamaterial characteristics that the collective surface nano-structures produce in its end application. Certain surface topology and geometric physical
estimates can be provided, however, the measurements can be challenging at the nanoscale. Here, quantitative estimates of the circularity of basic nanohole and nanopillar structures are provided based on SEM images of the sample surfaces.

Using an image analysis software (IGOR Pro), the boundaries that define the edges of the circular embossed holes or the circular pillars are detected. Figure 7-18 shows three SEM images of nanopillars and nanohole arrays where the structure boundaries are detected by the image software based on pixel contrast. The boundaries are annotated by the software in red line markings, and numbered such that each individual element can be selected for analysis.
The circularity is a quantitative measure used to evaluate the geometry of any relatively circular structures. It is a commonly quoted metric in applications such as that for nanohole arrays in surface plasmon resonance based sensing [76].

The circularity, $Circ$, is defined,
where, a circularity of 1 indicates a perfect circle. It is a ratio of the perimeter of the structure to the area of structure. The larger circularity value, the more the perimeter deviates from being perfectly circular.

The three examples shown in Figure 7-18 include a nanopillar array from a quartz master stamp (TOP), an embossed nanohole array on a rough PET sheet (MIDDLE), and Au nanoholes milled by FIB (BOTTOM). Figure 7-19 further shows the initial surface roughness of the lower quality PET sheet (stationary grade) used in the exploratory embossing trials. The granular surface appear to be consisted of approximately 50 nm diameter small pellets that are closely connected to each other, where some collections form links as long as 500 nm. The nanoholes created using FIB are individually milled on a Au metal thin film on Si, where several milling passes involving multiple beam powers are required to produce the highly circular holes. Circularity estimates are calculated for the examples shown in Figure 7-18. A summary of results is given in Table 7-1. It is evident that the circularity of the embossed nanoholes (6 ± 2) is not as excellent as the FIB-milled (1.19 ± 0.03), however, the circularity of the pillar structures (1.4 ± 0.1) are quite close to the high quality FIB-milled hole structures. Further, both the pillar structures and the FIB-milled holes are visually highly circular. As for the embossed nanoholes, it can be seen that the original PET roughness from film grains contribute largely to the poor circularity in the estimates.
Figure 7-19: SEM image (top view) of the original surface of the lower quality PET sheets (stationary grade) used in the explorative embossing trials; the inset shows a higher magnification image of the granular surface contributing to the roughness.

Table 7-1: Summary of circularity estimates of the example structures shown in Figure 7-18, including nanopillars on quartz master stamp, nanoholes embossed on rough PET, and high quality FIB-milled nanoholes [76].

<table>
<thead>
<tr>
<th></th>
<th>Quartz Stamp Pillar</th>
<th>Embossed Nanoholes</th>
<th>FIB-Milled Nanoholes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circularity</td>
<td>1.4 ± 0.1</td>
<td>6 ± 2</td>
<td>1.19 ± 0.03</td>
</tr>
</tbody>
</table>

Evaluating the utility and practicality of a fabrication process is inherently objective at parts. The circularity estimates provide a quantitative measure to give additional insight to this evaluation. Combining several forms of assessments as discussed in the prior sections, a holistic approach can be considered in comparing the effectiveness in creating master and subsequent nano-structures following the conventional versus the fast fabrication process developed. In the following section, the
time and cost savings of the novel fast fabrication are further compared against the conventional methods.

7.4. Comparison of Conventional vs. Rapid Master Stamp Process

Comparing the fabrication process times between the fast fabrication process (rapid master stamp) and conventional processes provide additional insight into the utility and practicality of the new fabrication flow developed. As discussed previously (Chapter 2.4), conventional EBL processes for creating nanopillar surface structures on hard substrates include:

- the bi-layer positive resist lift-off process [124], and
- the negative resist pattern transfer process [125].

In the negative resist pattern transfer process, the final height of the nanopillars attainable on the hard substrate is largely limited by the thickness of the negative resist. Often the etch resistance of the negative resist is only as resilient as the hard substrate beneath or much worse. In contrast, the bi-layer positive resist lift-off process applies a metal mask that is much more etch resistant when directionally etching the final pillars. In a basic comparison, only the conventional bi-layer positive resist lift-off process is compared against the novel fast fabrication process.

Table 7-2 below summarizes the comparison of the time and cost of conventional nanohole patterning versus the fast fabrication process (Step 2 of Figure 5-3). The structures considered in the comparison are basic nanohole arrays arranged in square lattice with a periodicity of 520 nm, and target hole diameters of 200 nm. The same EBL patterning tool (Raith ELine) is assigned for both processes, and the configurations are identical: 30 µm aperture, 10 keV beam energy, and 200 µm write-field. As the patterned nano-structure area increases from 1 cm$^2$ to 5 cm$^2$, the time and cost savings become drastically more meaningful. The corresponding cost savings increase from thousands of dollars to tens-of-thousands of dollars. For rapid prototyping of surface nano-structures, a total pattern area of 1 cm$^2$ can be completed within 24 hrs using the new process rather than 3 days as required by conventional writing using the same tool parameters.
Note that even with faster EBL writing settings, the fast fabrication process correspondingly improves the throughput by reducing the patterning time needed. The patterning time optimization is predominately limited only by the machine hardware scanning speed. The subsequent process steps in the fast fabrication process (Steps 3 to 9 of Figure 5-3) can be completed within a relatively short time, requiring only a few additional hours to arrive at out-of-plane nanopillar stamps.

**Table 7-2: Tool time and cost required for patterning large surfaces with nanoholes.** The nanohole arrays considered are arranged in basic square lattice, spaced 520 nm apart, targeting a final hole diameter of 200 nm. The patterning time and cost is based on the Raith eLine EBL tool operated with 30 µm aperture, 10 keV beam energy, and 200 µm write-field. A typical tool usage cost of $100/hr is applied [76].

<table>
<thead>
<tr>
<th>Surface area (cm²)</th>
<th>Time Required Using Fast Fabrication (h)</th>
<th>Cost Required Using Fast Fabrication ($)</th>
<th>Time Required Using Conventional Fabrication (h)</th>
<th>Cost Required Using Conventional Fabrication ($)</th>
<th>Difference ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21</td>
<td>2,100</td>
<td>75</td>
<td>7,500</td>
<td>5,400</td>
</tr>
<tr>
<td>2</td>
<td>42</td>
<td>4,200</td>
<td>150</td>
<td>15,000</td>
<td>10,800</td>
</tr>
<tr>
<td>5</td>
<td>105</td>
<td>10,500</td>
<td>375</td>
<td>37,500</td>
<td>27,000</td>
</tr>
</tbody>
</table>

In Table 7-3, the comparison is extended to include the total time required in the processes to arrive at final pillar structures on the hard substrates beneath the resist and process layers. In the fast fabrication process, two metal deposition cycles are required, one for the metal process layers, another for the Cr metal mask. In the conventional bi-layer liftoff process, two metal deposition cycles are also required, one for the thin metal film on the substrate beneath the EBL resists, another for the hard metal mask for lift-off. Each of these process steps would add 4 to 6 hrs to the overall fabrication time. The comparison further includes the conventional negative resist pattern transfer process. Here, the negative resist is assumed to have adequate etch resistant, even as effective as a metal mask. With such assumption, the negative resist process only requires one metal deposition cycle for the thin metal film on the substrate beneath the EBL resist.
Table 7-3: Summary of additional and total processing times for the fast fabrication process, the conventional bi-layer lift-off process, and the conventional negative resist process [76].

<table>
<thead>
<tr>
<th>Additional Process Steps</th>
<th>Processing Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rapid Fabrication Process</td>
</tr>
<tr>
<td>Metal deposition</td>
<td>6 + 6</td>
</tr>
<tr>
<td>RIE pillar etch</td>
<td>2</td>
</tr>
<tr>
<td>Liftoff</td>
<td>2</td>
</tr>
<tr>
<td>Resist development and/or chemical etching</td>
<td>1</td>
</tr>
<tr>
<td>TOTAL (additional)</td>
<td>17</td>
</tr>
<tr>
<td>TOTAL (including EBL time for 1 cm² pattern area*)</td>
<td>38</td>
</tr>
<tr>
<td>TOTAL (including EBL time for 5 cm² pattern area*)</td>
<td>122</td>
</tr>
</tbody>
</table>

* For nano-structures same as that described in Table 7-2

The processing times for the remaining steps in the fast fabrication process include:

- chemical etching, approximately 1 hr including handling time,
- RIE pillar etch, approximately 2 hours including setup and pump-down time,
• liftoff, approximately 2 hours.

Thus, a total of 17 hrs of additional post-EBL processing time is required for the fast fabrication process.

The conventional bi-layer liftoff process requires almost the same, 15 hrs (where the thinner initial metal layer beneath EBL resist requires shorter deposition time). The conventional negative resist patterning requires only additional 7 hrs.

In summary, when considering a nanopillar array area spanning 1cm² (pattern as described previously) an additional 17 hrs is required in excess of the 21 hrs of EBL patterning time, totalling 38 hrs for the fast fabrication process. An additional 15 hrs is required for the conventional bi-layer liftoff method, totalling 90 hrs. An additional 7 hrs is required for the conventional negative resist method, totalling 82 hrs. It is evident that while the additional process times are not negligible, it certainly does not reduce the percentage of time and cost savings comparing the fast fabrication versus the conventional processes by much. Particularly, when even larger pattern areas are considered, the throughput of the fast fabrication is noticeably far superior.

The time and cost comparison, along with the assessment of the nanohole and nanopillar structure circularity, as well as the variety of pattern arrangements and shapes demonstrated, combine to provide technologists a more thorough perspective of the utility and practicality of the fast fabrication process. In the following chapter, exemplar end applications enabled by surface nano-structures are discussed to further demonstrate the roles of master stamps and high volume replication in flexible advanced electronics.
8. Selected Application with Surface Nano-Structures

8.1. Integrated Bio-Chemical Sensing

8.1.1. Integrated Sensors

The ever increasing contributions of sensors to improving quality of life is undeniably profound. From those found in cellular phones to those inside car engines, sensors are very much a part of everyday life. Integrated sensors, sensors that are combined with microelectronic computing in a single substrate or package, dates back almost as far as integrated circuits themselves, and have made a remarkable journey thus far since the first investigations dating back to the 1950’s [126],[127]. It is evident that the advancement of integrated sensors technology is closely related to the innovations in electronic circuit technology. In the recent years, the cost of silicon based electronics have steadily decreased due to progressive improvements in global knowledge in fabrication and design. Thin film transistors disposable on flexible substrates and low cost printable electronics of many varieties [128]-[132] have further combined to motivate ubiquitous deployment of more integrated sensors in every industry and in applications or new forms. Today, low cost integrated sensors of many types can be architected so compact, light weight, and at times feasible on flexible substrates, such that its consequent portable instruments do in fact fit in the palm of a hand and that its disposable devices are in fact economical.

When integrated sensors are able to evaluate and process the data it gathers prior to releasing it to another device or storing the information, the integrated sensor is known as a smart sensor. With portability, mobility, and autonomy gaining increasing importance in many applications, often, smart sensors are designed to communicate wirelessly to a larger overall system to relay its information. Figure 8-1 illustrates a conceptual example of a wireless smart sensor system. The system is based on a smart
sensor patch that can be worn on the human skin much like a bandage. The sensor patch is light weight, mechanically flexible, soft, conforming, and low cost. In this example the smart sensor patch is a drug chemical detection patch that analyses the human perspiration through the skin.

![Smart drug sensor patch](image)

**Figure 8-1:** A conceptual wireless sensor system based on a wearable drug detection smart sensor patch.

The digitized and partially processes data from the smart sensor patch is wireless transmitted to a receiver. In Figure 8-1, two receiver paths are shown: 1) direct transmission to a backend database computer for extended processing or storage, or 2) transmission through an intermediate device prior to release to database server. The intermediate device could be a mobile computer-phone or specialized custom receiver router nodes. Portable, wearable, smart sensors like that in the conceptual example shown are becoming increasingly popularly investigated; however, in order to meet the unique form-factor, power consumption, and sensitivity requirements to name a few, both the integrated electronics and sensor components must become increasingly miniaturized. Figure 8-2 illustrates an example of an integrated smart microsensor assembly. This particular smart microsensor represents a conceptual bio-chip for transdermal drug detection. The smart microsensor assembly depicted here contains two subsystem moduals assembled in a stacked configuration: Figure 8-2-a represents the integrated electronics portion of the smart microsensor, where small micro-chips and application circuit components are disposed on a single carrier substrate or a series of layers (e.g. a multilayer platform [133]-[138]). The integrated electronics could contain
sensor signal amplification and conditioning, conversion to digital signal, microprocessing, and wireless transmission capabilities. Figure 8-2-b represents the sensor detector portion where the extraction of the analyte sample, processing and handling of sample, identification of target species, and transduction of signal takes place. In this transdermal sensor example, a set of micro-needles protrude from the surface of the microchip where microfluidic channels siphon the fluid samples into analytic chambers where the transduction takes place. The mechanism of transduction could be based on chemical bonding, optical-spectral, or magnetic properties of the analyte to name a few. Figure 8-2-c shows the complete microsensor assembly, while Figure 8-2-d shows the possible wearable configurations on a subject for transdermal drug-chemical detection, as a disposable wrist contact band or a skin patch.
Figure 8-2: Conceptual configuration of a multilayer integrated smart microsensor bio-chip for transdermal drug detection. A) the microelectronics subsystem layer(s); B) the front-end extraction and sensor subsystem layer(s); C) the assembly of the smart microsensor; D) the possible wearable forms of the integrated smart microsensor.

Figure 8-3 gives an example of the subsystem blocks on a multisensor platform [134] to implement the integrated electronics for a smart microsensor as that depicted in Figure 8-2-a. In this design, the multisensor platform accommodates several sensor input channels “simultaneously” in a way where multiple input signals are acquired sequentially one-after-another (e.g. round-robin scheme) at a sufficiently rapid rate relative to the variations in the signals of interest. For example, if there are three sensors, each transducing signals from the analyte with a maximum variation of 500 Hz, then by Nyquist theorem each sensor channel must be sampled at higher than 1 kHz. Hence, the overall sampling rate of the analog to digital (A/D) signal converter must be operated at greater than 3 kHz. Common low-cost microchip A/D signal converters available today are capable of sampling at rates much higher than several kHz. The multisensory platform further includes a set of computer switchable analog filters such that any filter bank can be applied to any sensor depending on the application requirements without an overwhelming number of circuit components. The transduced
signals from the sensors are passed through the signal filters and conditioning units, digitized by the high speed A/D converter, and received at the microprocessor (or microprocessing unit, MUC). The microprocessor may contain on-chip memory storage such that small amounts sensor data can be retained. Often, to reduce the burden and activity, and hence the power consumption of the smart sensor, the microprocessor may make calculations based on the sensor signals, and based on the results of those calculations, make a decision to transmit a summary of the data to a backend receiver.

![Figure 8-3: Subsystem blocks of the integrated electronics on a multisensor platform for smart microsensors [134].](image)

Figure 8-4 gives another example configuration of a front-end sensor subsystem for a self-powering smart microsensor. In this example, a mechanical energy harvesting material is incorporated into the sensor assembly such that a micro light source can be powered and illuminated for opto-microfluidics chemical sensing [133]. The subsystem is assembled in a 3D stacked configuration. A microfluidics layer containing microchannels where liquid sample analytes are passed through is attached above an OLED layer. Small arrays of micro OLEDs are patterned on a thin substrate and aligned beneath the microchannels so to provide excitation illumination in a possible variety of optical analysis. Fabrication of arrays of OLEDs are well studied [139]-[145], but a basic procedure for preparing OLEDs is also given in Appendix C. A polyvinylidene fluoride (PVDF) mechanical energy harvesting film stack [133],[146],[147] is inserted beneath the microfluidic and OLED layers. Lastly, a series of Nafion based ionic-polymer-metal-composite (IPMC) energy storage films [133],[148],[149] in essence like soft polymer batteries [150], is attached beneath the energy harvesting layer. The electrical connections can be made by printed circuit wirings and through the various layer by
interconnects [151]-[155]. The overall multilayer stacked assembly can be less than a millimeter thin.

Figure 8-4: Example configuration of a front-end sensor subsystem for a self-powering smart microsensor based on opto-microfluidics for optical types of chemical sensing [133].

The subsystem blocks for powering the OLED of the front-end portion of the self-powering smart microsensor illustrated in Figure 8-4 is further depicted in Figure 8-5. The flow of the harvested energy begins with the conversion of mechanical energy input to electrical energy via the pressure sensitive PVDF film. A charge circuit then rectifies the AC input into DC where then the electricity is accumulated into the IPMC energy storage films. A power regulator controls the energy required from the IPMC storage films and other possible complimentary power sources to activate the OLED arrays. Other system components such as the photodiode detector (not shown here), can be powered in this manner alike. A preliminary proof-of-concept system following what’s described has been demonstrated to be able to power micro OLEDs from small amounts of human mechanical actuation [133].
When low-cost energy harvesting solutions can be incorporated into smart microsensor systems, a multitude of very useful and exciting applications awaits. Figure 8-6 depicts a conceptual single-use advanced oral swap smart microsensor system for drug-use detection. A smart microsensor device can be made such that it can harvest sufficient mechanical energy from a brief series of actuations, perhaps like that described in Figure 8-5, to administer a single set of analyte tests. The smart microsensor can then relay information on the assessed results to a wireless data receiver upon request. The wireless data return transmission from the smart microsensor can also be assistively powered by wireless energy bursts transmitted together along with the original request for data from receiver device. Because the traditional battery source is eliminated, and the analyte detection is completely administrated by the smart microsensor such that no additional specialized equipment is required, several key cost factors are eliminated. A larger number of tests and more sophisticated assessments (as opposed to passive sensors) can be carried out at more locations that are previously unattainable. However, every component of a smart microsensor system must possess favorable cost economy. As such, sensors that require sophisticated nano-structure arrays are often limited by its fabrication costs. In
the following section, low cost nano-structured surfaces for a unique type for sensing is examined, and its role in integrated smart sensors are discussed.

Figure 8-6: A conceptual single-use advanced oral swab smart microsensor system for drug-use detection.

8.1.2. Nanohole Arrays for Surface Plasmon Resonance Based Sensing

For over a few decades, scientists have used surface plasmon resonance (SPR) to detect local refractive index changes and chemical binding events [156]. In the early 1980’s, SPR based applications extended further into bio-chemical sensing [157]. Some of the exceptional qualities of SPR based bio-chemical sensing were that it is chemical label free and highly sensitive to surface variations [158]. The apparatus for SPR based sensing prior to the late 1990’s consisted of the Kretschmann geometry, which required a light prism [158]. This setup involving a light prism gave an extremely high detection limit of approximately 10 pM, corresponding to $3.0 \times 10^{-8}$ refractive index units (RIU). However, the bulkiness and physical size of the light prism did not allow for easy miniaturization. In 1998, Ebessen et al. [159] demonstrated a phenomenon known as Extraordinary Optical Transmission (EOT), which was an unique transmission of light mediated by SPR through an array of subwavelength nanoholes in a thin but optically opaque metal film. Based on Ebessen’s earlier works, the recent decade of research in this area explored the use of surface nanohole arrays in miniaturized bio-chemical
sensing. In 2004, Brolo et al. demonstrated the use of nanohole arrays to monitor biochemical binding events in a laboratory setting [160]. This new generation of SPR based sensing technique inspired several efforts in exploiting the possibilities of integrating such surface nano-structures in small sensors with microfluidic chips for a variety of portable, low-cost, industrial and health solutions. Over the past decade, as nanofabrication technology improved in parallel, more and more researchers were able to demonstrate a variety of integrated micro-optical-sensor systems housing sensor chips that contained surface nanohole arrays [18],[161],[162]. However, the cost and throughput for fabricating such nano-structures (as described in several earlier chapters) remains a challenge, particularly for more advanced sensor designs that require mixed arrangements of nanohole arrays.

Figure 8-7 shows an exemplar sensor platform for SPR nanohole array based bio-chemical sensing [113]. The sensor platform can be incorporated with electronic subsystems (e.g. Figure 8-3) to form a complete integrated microsensor device (e.g. Figure 8-2) for use in mobile or portable low-cost sensor solutions (e.g. Figure 8-1, Figure 8-6). The sensor platform consists of three core components arranged in a stacked configuration: 1) a microfluidic layer that transports small amounts of analyte across the sensing sites; 2) a sensor layer containing surface nanohole arrays; and 3) a source lighting layer containing white-light OLEDs.
The configuration shown in Figure 8-7 places the sensor layer in between the microfluidic layer over top, with the source light layer beneath. The microfluidic layer contains inlets where the sample can be injected into the microchannels and transported across several surface nanohole arrays by capillary action. In such way, the liquid analyte in each microchannel comes into direct contact with a battery of nanohole array sensor sites, providing a more comprehensive SPR based analysis than sensor systems containing only one single nanohole array type [113]. The OLED layer is placed beneath the sensor layer such that the illuminating pixel strips are located directly beneath each nanohole array. The location of the illuminating pixels can be strategized to reduce scattering and noise from ambient light. Incorporating a source lighting layer eliminates the requirement of an external light source, which often brings extra complexity and significantly heightened cost relative to the remainder of lab-on-chip components [5]. The sensor platform thus only requires the additional power source for the OLED layer (perhaps via self powering by incorporating that shown in Figure 8-4 or a small soft battery pack [150]), a spectrometer detector system (perhaps a small integrated assembly [5]), and a data-logging computer (if not incorporated into a smart sensor system already).
The design of the SPR nanohole array integrated sensor platform seems feasible given that numerous accounts of integrated microfluidic sensor chips have been demonstrated in the past [163]-[166], and that both low-cost microfluidic and OLED technologies are relatively well-established. As such, what remains to be demonstrated is whether the flexible nanohole arrays on thin plastic substrates created through the low-cost rapid techniques presented in this work provides sufficient sensitivity for useful application or not. In the following section, SPR sensing characteristics of the low cost embossed nanohole array samples created in this work are examined.

8.1.3. **SPR Sensing Characteristics of Low-Cost Nanohole Arrays**

Embossed nanohole arrays are studied to assess its optical characteristic for SPR based bio-chemical sensing. The test arrays are created on the surface of thin PET sheets. The polymer embossing replication techniques follows that described in Chapter 6.1. The master quartz stamp applied is originated using the fast fabrication process described in Chapter 5. The arrays studied contain nanoholes arranged in square lattice, like that shown in Figure 7-14. Once the nanohole indentations are created on the surface of the polymer, the array regions are coated with 5 nm of Cr and then with 100 nm of Au. The thin film coating process is by thermal evaporation. The Cr acts as an adhesion layer to improve the attachment of the Au film to the surface of the polymer nano-structures. Note that unlike traditional SPR nanoholes milled by FIB, which are through-holes, the Au film on the polymer nanoholes coats the entire surface including the base of the nanoholes. Figure 8-8 illustrates this difference between embossed thin film nanoholes (LEFT) and traditional FIB-milled nanoholes (RIGHT).
One form of SPR based sensing is determining the presence of a chemical species by detecting relative changes in the nanohole transmission spectra. The sensitivity of the nanohole array can be related to the shift in the array’s EOT resonance peak as the analyte’s refractive index changes. Figure 8-9 shows a simplified diagram of a transmission measurement setup [113]. Here, a halogen white light source is focused through a microscope objective onto a nanohole array under study. The transmitted light is coupled through a fiber optic cable to a spectrometer (Photon Control SPM-002-C with custom range 500-1000 nm). The recorded spectrum is an average of twenty 200 ms exposure acquisitions. The background spectrum is the transmission through an area of the Au coated sample without nanohole arrays. The samples contained four different periodicities, ranging from 500 to 625 nm.
The wavelengths of the EOT peaks are predicted by,

\[ \lambda_0 = \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d \left( \frac{a}{\lambda} \right)^2}} \]

(8-1)

where \( a \) is the periodicity of the array, \( ij \) are integers describing the order of the resonance, and \( \varepsilon_m \) and \( \varepsilon_d \) are the dielectric functions of the metal film and the dielectric substrate respectively [159][167]. In reality, the EOT peaks are expected to be red-shifted from their predicted location because Equation 8-1 does not consider parameters such as directly transmitted and scattering light, hole shapes, and hole sizes [168]-[169][171].
Figure 8-10 shows the background subtracted transmission spectra in air for the embossed nanohole arrays [76]. For clarity, only every eighth data point on the spectra is plotted. The locations of the prominent [1, 0] Air-Au transmission peaks are further marked by arrows. The peaks show a direct dependence on the array periodicity, as predicted by Equation 8-1. Further, the peaks shift to higher wavelengths with increasing array periodicity. The EOT peaks are a combination of SPR resonance and directly scattered light. This combination of transmission gives the measured peaks a characteristic asymmetric shape.

![Typical transmission spectra for four different square lattice nanohole arrays. The periodicities range from 500 to 625 nm. The prominent [1, 0] Au-Air EOT peaks associated to each periodicity are individually marked by arrows. The inset compares the typical spectrum of the embossed 550 nm periodicity nanohole array with that of the FIB-milled (more accurately machined) nanohole array [76].](image)

The inset in Figure 8-10 shows a comparison of the typical background subtracted transmission for an embossed nanohole array and a FIB-milled nanohole array of the same periodicity (550 nm) and arrangement (square lattice). The FIB-milled arrays are prepared by collaborating researchers (D. Hohertz from the SFU Kavanagh Physics Research Group). The embossed PET-Au nanoholes have hole diameter of 250 ± 20 nm. The FIB-milled glass-Au nanoholes have hole diameter of 124 ± 4 nm. Because FIB-milling of the nanohole arrays is rather time consuming, smaller area arrays are examined compared to larger embossed arrays. The spectra are
consequently scaled to account for differences in the total number of nanoholes in each comparative samples.

The transmission peaks seen at approximately 540 nm and 569 for the embossed arrays on PET and 547 nm for the FIB-milled array on glass correspond to the [2, 1], [2, 0] Au-PET and [2, 0] Au-glass resonances, respectively. The transmission peaks at 628 nm for the embossed arrays and 638 nm for the FIB-milled arrays are the [1, 0] Au-air resonances for both. Lastly, the peaks at 746 nm for the embossed arrays and 701 nm for the FIB-milled arrays are the [1, 0] Au-PET and [1, 0] Au-glass peaks, respectively. There is a noticeable approximate 10 nm difference between the locations of the [1, 0] Au-air resonance peaks for the embossed nanohole arrays versus the FIB-milled arrays. It is likely that the geometry differences (e.g. Figure 8-8) and various fabrication inaccuracies leading to slight lattice mismatches between the embossed and FIB-milled arrays contributed to the difference. In between the [2, 0] Au-substrate and the [1, 0] Au-air peaks, a series of minima attributed to Wood’s anomalies [159] are observed. The full width half maximum (FWHM) of the two [1,0] Au-air peaks are similar: 30 ± 1 nm for the embossed versus 27 ± 2 nm for the FIB-milled.

The magnitudes of the resonance peaks are very different in the embossed versus FIB-milled arrays. The greater surface roughness of the PET substrate, and subsequently translated to the Au film coating (roughness 50 ± 25 nm), compared to the more finely FIB-milled Au (roughness 16 ± 4 nm) may have reduced the EOT resonance by allowing scattering and radiative decay of the SP modes [172]. Further, the nature of the metal film deposition on the embossed arrays is such that it also coats the bottom and sidewalls of each indented nanohole cavity, as described in Figure 8-8. It has been verified and reported through computer simulation that thicker metal film coatings on the sidewalls of nanohole cavities correspond to higher attenuation to the EOT light [76].

The distinct [1,0] Air-Au EOT peaks shown in Figure 8-10 validate that while the quality of the embossed nanohole arrays on PET may not be as excellent as the finely FIB-milled holes, the embossed nanohole arrays can in fact generate significant SPR containing the same characteristic EOT resonance peaks as that of the FIB-milled array. Although the resonance intensity is approximately an order of magnitude lower, the resonance peaks are clearly detectable and identifiable when the appropriate light
source and detectors are applied. Given the vast selection of electronic hardware available in today’s technology, it can be expected that even at lower intensity, without further optimization of the polymer surface and metal film coating, such embossed nanohole arrays can potentially be practical sensor elements in low cost SPR based sensing.

To further assess the sensitivity of the embossed nanohole arrays to changes in bulk refractive index of an analyte solution, aqueous glucose solutions with varying concentrations are examined [113]. The glucose solutions are deposited on top of the nanohole arrays in the same setup as that shown in Figure 8-9. The refractive indices of the glucose test solutions are verified using an Abbe Refractometer, at 22°C, prior to the nanohole measurements. Figure 8-11 shows the EOT spectra of an embossed nanohole array exposed to different glucose solutions of varying concentrations. The nanohole arrays are configured in basic square lattice with a 675 nm periodicity. For clarity, the graph is cropped to focus on the [1,1] solution-Au resonance peak. The black arrows mark the locations of the resonance peaks.
Figure 8-11: Typical red-shift of the [1,1] solution-Au EOT peak of an embossed nanohole array (square lattice, periodicity 675 nm) with increasing refractive index. The black arrows indicate the locations of the EOT maxima. The transmitted intensity decreases as the peak red-shifts due to the intensity profile of the incident light source. The transmitted light intensity at 710 nm is approximately 0.5 ± 0.1% of the total incident light [113].

As the glucose concentration and consequently the refractive index increases, there is a red-shift in the EOT peak as predicted by (8-1). The transmitted intensity decreases as the peak red-shifts because the intensity profile of the incident light source diminishes at higher wavelengths. The peak locations are identified and summarized in Table 8-1.

Table 8-1: Locations of the shifted [1,1] solution-Au EOT peaks of the embossed nanohole arrays (square lattice, periodicity 675 nm) corresponding to the various glucose solutions and refractive index [113].

<table>
<thead>
<tr>
<th>Concentration of Glucose Solution (M)</th>
<th>Refractive Index of Glucose Solution</th>
<th>Location of Shifted [1,1] solution-Au EOT Peak (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.347</td>
<td>708 ± 3</td>
</tr>
<tr>
<td>1.0</td>
<td>1.359</td>
<td>713 ± 4</td>
</tr>
<tr>
<td>1.5</td>
<td>1.372</td>
<td>715 ± 4</td>
</tr>
</tbody>
</table>
Four additional exemplar embossed nanohole arrangements are examined. The arrays are also arranged in basic square lattice, and vary in periodicity from 650 nm down to 525 nm. Figure 8-12 shows the maxima positions of the [1,1] solution-Au EOT peaks as a function of refractive index for the five different embossed nanohole array arrangements. The maxima positions are also given for a typical FIB-milled nanohole array arranged in square lattice with a periodicity of 550 nm. It is clearly evident that the resonance peak positions shift towards higher wavelengths as the array periodicity increases. The resonance peaks of the FIB-milled arrays (marked by green diamonds) are red-shifted from those of the corresponding embossed arrays (marked by green bow ties). The variation is likely due to the differences in the hole geometries arising from the different fabrication procedures (as described earlier in Figure 8-8). The peak data-points are fitted to a line to extract the slope, which represents wavelength change in peak position as refractive index changes. This relationship is the sensitivity of the nanohole array SPR based sensor.
Figure 8-12: SPR [1,1] Au-solution peak position versus refractive index for five embossed nanohole array types (square lattice, various periodicities). The slope of the fitted lines represent the peak wavelength shift per refractive index unit, and describes the sensitivity of the nanohole array SPR based sensor. The embossed arrays show the same direction of slope compared to the higher quality finely FIB-milled nanohole arrays. The SPR peak red-shifts as the array periodicity increases [113].

The sensitivities of the various embossed nanohole array arrangements and the representative FIB-milled array are summarized in Table 8-2. It is noticed that the FIB-milled array demonstrates 25% higher sensitivity than the corresponding embossed array with the same periodicity. This variation may be attributed again to the increased surface roughness on the PET substrate compared to the glass substrate, and the inherently different hole shapes (Figure 8-8). The embossed nanohole arrays demonstrate an average sensitivity of approximately 180 nm/RIU. This implies that a 1 nm shift in the SPR peak location occurs with a refractive index change of approximately $6.0 \times 10^{-3}$ RIU. This is equivalent to changing a liquid solution from pure water to a glucose solution with concentration of approximately 0.2M. Note that it is common for inexpensive spectrometers to have resolution higher than 1 nm. As such, although the first generation of embossed arrays seem less sensitive than the finely FIB-milled nanohole arrays, they can be quite effective in “on-off” types of detection: for example, for full monolayer absorption of large biological molecules [160] or to monitor large changes in aqueous solutions. However, without further improvements, the embossed
nanohole arrays would likely not be effective for low concentration gas sensing applications where the low molecular density of the gases result in even more minute changes in refractive index [173].

Table 8-2: Summary of the sensitivity or “shift per refractive index unit” of the various embossed and milled nanohole arrays corresponding to the data shown in Figure 8-12 [113].

<table>
<thead>
<tr>
<th>Periodicity (nm)</th>
<th>Sensitivity Shift/Refractive Index Unit (nm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>675</td>
<td>190</td>
</tr>
<tr>
<td>650</td>
<td>240</td>
</tr>
<tr>
<td>625</td>
<td>100</td>
</tr>
<tr>
<td>550</td>
<td>250</td>
</tr>
<tr>
<td>525</td>
<td>120</td>
</tr>
<tr>
<td>Milled 550</td>
<td>310</td>
</tr>
</tbody>
</table>

Based on the sensitivity results summarized in Table 8-2, there seems to be no unique relationship between the periodicity of the arrays and the magnitude of the sensitivity. This observation suggests that there may be sufficient inconsistency in the embossed nanohole arrays sampled for the study, and that a larger set of data may provide deeper insight on the average sensitivity. In general, the lower sensitivity in the embossed nanohole array could be largely due to the holes being are less circular (Chapter 7.3) and the granular PET substrates leading to higher surface roughness. The surface roughness and the hole circularity can be improved by post-embossing surface treatments, or by replication with higher precision UV-casting.

The embossed nanohole arrays exemplify that replicated nano-structures can be suitable sensor elements in applications such as SPR based bio-chemical sensing. The fast fabrication process for master stamps, combined with the variety of high volume
replication processes presented earlier in this work, further indicate that surface nano-
structures replicated on thin polymer substrates can play a significant role in bringing
cost effective solutions to integrated microsensors that require nano-optical elements.
While several areas for improvement still lay ahead in replication technologies for nano-
structures, the methodologies and results demonstrated in this work contribute
incrementally to the pool of knowledge in the community concerned with creating large
area high volume nano-structures on thin polymer substrates for applications in sensors
and flexible electronics.
9. Contributions

9.1. Summary of Selected Journal Publications

1. [SJ#1]

   This journal publication in Institute of Physics (IOP) Nanotechnology (impact factor 3.979 in 2011) is the first to report on the novel fast fabrication method for originating circular nano-structured master stamps from this work. The article discusses the limitations in conventional fabrication methods in creating multiple arrangements of surface nano-structures on a single master stamp substrate (from Chapter 2 of this work). The methodology of the fast fabrication process is introduced and demonstrated (from Chapter 4, 5, and 7 of this work). The analysis shown for the throughput suggest greater than 3 X improvement in original patterning time (from Chapter 7 of this work). A preliminary study on the EOT spectra through exemplar replicated nanohole arrays is also given to validate the utility of the master stamp process (from Chapter 8).

   Within the first month of publishing, the paper has received more than 100 downloads according to IOP’s online metrics.

   The specific author contributions are as follows: Y.C. conceived the method for the rapid fabrication of nano-structured master stamps, developed the processes, and carried out the experiments. C.L. and B.O. developed the foundation knowledge in the use of conventional direct-write tools for nano-
patterning, and carried out the embossing. D. H. carried out the SPR sample characterization and analysis. B.O. carried out the SPR model simulation and analysis. S. G. assisted in experiments for the rapid fabrication process. Y.C., C.L., B.O., and D.H. wrote the manuscript. B.K. and K.K. edited the manuscript and supervised the work.

2. [SJ#2]

This journal submission to a Special Issue on Flexible Sensors in IEEE Sensors Journal is a follow up to the potential applications for the technologies disclosed in SJ#1. This is the first to report on the sensitivity of the embossed nanohole arrays using the rapid master stamps for possible use in SPR based bio-chemical sensing (from Chapter 8 of this work). The quality of exemplar R2R high volume replicated nanohole arrays using the master stamps are also presented for the first time (from Chapter 7 of this work). An integrated microsensor platform combining a microfluidics layer and OLED illumination to the nanohole array SPR sensor elements is discussed (from Chapter 8 of this work). The type of low cost, flexible, polymer substrate based sensor platform presented is a current topic of high interest to a large community of electronics engineers.

3. [SJ#3]
This journal article presents the design and implementation of an integrated sensor platform with energy harvesting mechanisms to self-power optical illumination for micro-sensing (from Chapter 8 of this work). The sensor platform is configured in a thin 3D stack. The component layers are lightweight and mechanically flexible. The article discusses powering a thin polymer light source sufficient for microfluidics and nano-optics based bio-chemical sensing for the first time (from Chapter 8 of this work). It is demonstrated that only a small amounts of human mechanical input is needed to power the micro components in consideration. The physical attributes of the thin sensor platform makes it attractive to several other applications in low-cost sensing.

This article was invited for submission in the IEEE Sensors Journal as one of the top papers selected from the IEE Sensors 2010 Conference.


This journal article presents an integrated sensor platform that include multiple sensors on a single compact node. The underlying architecture contain electronic subsystems that are capable of amplifying, filtering, acquiring, digitizing, processing, and wirelessly transmitting the sensor information (from Chapter 8 of this work). The platform design is fundamental to the derivation of subsequent integrated microsensor architectures such as that in SJ#2 and SJ#3.

### 9.2. Summary of Selected Patents

1. **[SP#1]**

This patent application discloses the methods and techniques for faster fabrication of surface nano-structures for originating master stamps (from Chapter 4, 5 of this work). Detailed fabrication steps, materials, and a variety of process considerations are presented. This report shares the novel method with the community of users, while protecting its rights for commercialization interests.

Y. Chuo is the main inventor of this work.

2. [SP#2]

B. Kaminska, C. Landrock, Y. Chuo “Flexible polymeric light emitting/charge storage device and system,” U.S. Patent 8,212,473, issued July 3, 2012 (Main inventor)

This patent (granted) discloses the architecture of a polymer-based light emitting device that is integrated with a soft polymer energy storage source (from Chapter 8 of this work). The energy storage source can possibly also act as an energy harvesting source. A variety of micro and nano-optics can be also integrated onto the thin stacked architecture of this technology.

Y. Chuo is the main inventor of this work.

The patent was granted with virtually no revisions needed.

9.3. List of all Relevant Publications

Below is a complete list of all relevant publications produced directly or indirectly from and during the course of this work. The reported work include discussions on integrated sensor architectures, flexible electronics, R2R fabrication of polymer electronics, fabrication of nano-structures, nano-sensors, and soft-packaging. The selected key publications and patents discussed earlier is highlighted in grey colouring.
Refereed Journal Articles (Key Publications Highlighted)


Fully Refereed Conference Articles


Abstract Only Refereed Conference Articles


Technical Magazine Articles


Other Technical Articles


Book Chapters


Patents (Key Publications Highlighted)


10. Future Work

The novel fast fabrication process in this work provides a technique in creating nano-structured master stamps more efficiently than the conventional. In general, an improvement of approximately 3 X is achieved, where a larger improvement is observed for larger pattern areas, and a slightly smaller improvement is observed for pattern areas smaller than 1cm². While the fabrication throughput can be estimated for any design pattern and size based on existing data and process parameters, most experiments executed to date are based on standard EBL beam settings on a single EBL tool (Raith ELine). As previously described (Chapter 5.3), a proportional improvement in patterning time is expected to correspond to the optimization of the EBL beam settings. Studying the improvements of the fast fabrication over the conventional through a larger demographic of EBL patterning settings and (perhaps) equipments will provide a more thorough insight on the value of the novel fabrication process. For example, a number of higher beam apertures and larger write-fields, executed on different EBL tools can be experimented.

The fundamental methodology in reducing the costly patterning time in the fast fabrication process is by patterning small initial structures on a layered surface, and then subsequently transferring and enlarging the structures to specific material layers beneath. The material layers of the process (Chapter 5.2) contains specific functions, including a writing-layer, pattern transfer layer, and a lift-off layer. The material for each of these layers can be selected from a large list of candidates, however, the selections must form compatible combinations with respect to the etching requirements as previously described (Chapter 5.1 and 5.2). An exemplar list of compatible process layer sets is given in Table 5-2, however, several alternatives exist. Particularly, lower-cost materials may further reduce the expenses of the fabrication process in conjunction with the time and cost savings already established. As such, it is valuable to study a larger variety of compatible fabrication process layers and substrates to extend the understanding and complete assessment of the fast fabrication process demonstrated.
The master stamps fabricated using the process show versatile circular pattern arrangements and a variety of hole and pillar structures. In several end applications for low cost nano-structured surfaces, individual elements with higher aspect ratios may be desirable. Currently, a limited analysis on the maximum hole depths for hard templates and pillar heights for hard stamps is available. Series of experimental studies involving tuning the RIE recipe and incorporating deep-RIE (DRIE) can provide the further insight into the maximum aspect ratios achievable using the mask layers in the fast fabrication process. The extended trials will also expand the capabilities of the fabrication process to enable a larger range of end applications.

The effectiveness of the stamps are verified through a different replication processes, including direct embossing and R2R high-volume replication. The resulting nano-structures replicated on polymer surfaces demonstrate excellent yield and consistency across large surfaces and large lengths. However, several other replication processes are not explored. In particular, a number of high-quality high volume UV casting techniques as well as emerging polymer casting of various assortments can be explored. Demonstrative studies on a larger selection of high volume replication processes will provide valuable insight on the compatibility of the hard stamps and templates created using the fast fabrication process with candidate manufacturing regimes for future user reference.

The utility of the stamps and replicated nano-structured surfaces are demonstrated through a specific exemplar application on integrated microsensors for SPR based bio-chemical sensing. This end application incorporates basic smart sensor platforms with low cost microfluidic, lighting, and sensor components enabled by the cost-improved nano-fabrication presented in this work. However, as discussed in the introduction to this report (Chapter 1.2), a vast range of several other applications can benefit from this same master stamp fabrication improvement. Some of these applications include electrode texturing for OLEDs, plasmonic optic components for OPV interfaces, and mould fabrication for dry adhesive nano-structures. Fabricating master stamps using the fast fabrication process, and subsequently incorporating the masters into the production regimes for each application will establish excellent case studies for supporting the utility of the process presented in the work.
11. Conclusions

This work presents a novel fabrication process for creating nano-structured master stamps that is faster than the conventional. These master stamps can be applied in replication production of large area surface nano-structures, economically, at high volumes. For several applications in flexible electronics and low cost sensors that require large areas of surface nano-structures, the cost for the component nano-elements has commonly been prohibitive. The fast fabrication process improves the throughput in creating master stamps, hence lowering the overall production costs. For the community of users who do not have access to the latest and fastest nano patterning tools, this fast fabrication process contributes to be pool of knowledge in the techniques available.

This report began by discussing the scale perspective of nano-structures. It presented a simple survey of exemplar applications of surface nano-structures. The fundamental approaches to creating surface nano-structures were discussed. A review of the state-of-the-art conventional fabrication processes for nano-structured master stamps was given. Through this review, the limitations of the conventional processes were identified. These discussions combine to help illustrate the motivation in developing a novel fast fabrication process for creating nano-structured master stamps. In particular, conventional fabrication could require several days to pattern a 1 cm² region of original surface nano-structures, a process much too long and costly for many applications. The methodology of the novel fast fabrication process was presented, followed by the detailed discussion of the process steps. Because the quick patterning is based on a single beam dot-exposure, the resulting structures are fundamentally circular. The concepts, techniques, cautions, and insight were given for each aspect of the fabrication process flow. A small selection of demonstrative replication processes using the master stamps were given and their techniques further discussed. Representative fabrication samples were given for both original masters and replicated structures. Notably, a variety of nanohole template and nanopillar stamps containing multiple arrays of different
arrangements were demonstrated. Results from high volume replication using a secondary master was presented. Both master stamps and replicated structures showed excellent nano-structure yield. Circularity comparisons revealed that the circular pillar structures on the master stamps were highly accurate, while the replicated hole structures were not as excellent, due to the inherent roughness of the polymer substrates. A cost saving comparison as given next, revealing generally a 3 X improvement in the fast fabrication process over the conventional. To validate the utility of the master stamp fabrication process, an exemplar application requiring large areas of economical surface nano-structures was chosen such that specific master stamps were required to produce high volumes of polymer samples by replication. A smart sensor containing an electronic subsystem, integrated microfluidics, polymer lighting, and SPR nano-optics was discussed. The final nanohole arrays produced on thin polymer sheets were characterized for its use in SPR based bio-chemical sensing. The resulting sensitivity values of the SPR nanohole arrays were adequate for on-off types of chemical detection. As such, the utility and practicality of fast fabrication for master stamps was demonstrated through lower-cost origination of the master, generating excellent yield in the high volume replication production of polymer surface nano-structures, and qualifying sufficient sensitivity for selected uses in SPR based bio-chemical sensing.

The fast fabrication process presented in this work thus demonstrated an addition to the pool of knowledge and techniques that contributed to the incremental improvement to the science and engineering of building surface nano-structures for flexible electronics and low cost sensors. This master fabrication process is recommended for originating surface nano-structures that exceed a total area of 1 cm$^2$ on any EBL and similar scan-types of lithographic patterning tools. The writing time savings enable designs containing larger areas of nano-features to be realized more economically and practically in meeting certain industrial throughput requirements and research concepts that cannot be demonstrated convincingly otherwise. For example, several applications in nano-optics based chemical or light sensors, colour displays, waveguides, and thermal emitters may require aperiodic, varying nano-patterns in their design, spanning a relatively large surface area. The fast fabrication method in this work can mitigate the costs of originating a master stamp or template compared to
conventional methods enabling more scientific and commercial participants to engage in this area of technology adventures.
References


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Appendices
Appendix A.

Additional Information on Key Fabrication Tools for Master Stamp Origination

Focused Ion Beam

The focused ion beam system employed in this work is the FEI Strata 235 Dual Beam SEM/FIB located at the Nanoimaging Facility at SFU. The tool has a single chamber and two primary columns, one for each of the SEM and FIB guns. As such, samples loaded in the chamber can be examined and treated by either the SEM or FIB interchangeably. Most of the SEM imaging in this research are conducted using the SEM on the Strata 235.

Below is a list of the basic SEM and FIB parameters for this tool:

Ion Column
- 10 – 30 keV
- 1pA – 20nA
- Ion source Ga+

Resolution 7 nm
- Electron Column
- 0.2 – 30 keV
- Resolution 3 nm
Detailed operation instructions are available through the nanoimaging training program.

**Electron Beam Lithography**

The EBL patterning in this work is performed on the Raith ELine EBL system located inside the 4D Labs Cleanroom. The tool is capable of achieving less than 20 nm minimum feature size. The electron beam energy is available from 100 eV to 30 keV through a thermal field emission source. The stage is controlled by laser-interferometry to provide nanometer precision.

Some common beam setting parameters include the following popular options:

- Beam energy: 5, 10, 20, 30 keV
- Beam aperture: 10, 20, 30, 60 µm
- Write field: 100, 200, 500, 1000, 2000 µm

Example settings that create 50 nm to 70 nm small spot-sized holes on 50 nm PMMA (950M) resist is as follows:

- Beam energy 10 keV
- Beam aperture 30 µm
- Resulting beam current approx. 0.20 nA
- Dose 0.01 pAs

Detailed operating procedures can be found through the 4D Lab website or by enrolling in the equipment training program.
Thermal Evaporation Physical Vapour Deposition

The majority of the thin metal film deposition in this work is performed on the thermal evaporation deposition tool designated as “PVD5” at the 4D Lab Nanofabrication and Nanoimaging Facility. Thermal deposition is a directional type of physical vapour deposition. As such, the step coverage of the sample surface may be poor, but useful in certain applications. This tool provides dual evaporation sources simultaneously for the option of co-deposition. A low vacuum pressure of approximately $3 \times 10^{-6}$ can be achieved typically within 1.5 hours of pump-down for non-polymer bulk substrates.

Two exemplar deposition recipes are given below:

**Au 50 nm Deposition (on PVD5 Source 2)**
- Current ramp to approx. 24 A
- Voltage follows to 3.7/3.8 V
- Initial rate at 0.1/0.2 Å/s, and steady rate at 0.4/0.5 Å/s

**Cr 50 nm Deposition (on PVD5 Source 1)**
- Power percentage ramp to approx. 40 %
- Current follows to approx. 40 A
- Initial rate at 0.1/0.2 Å/s, and steady rate at 0.3/0.4 Å/s

Detailed operating procedures can be found through the 4D Lab website or by enrolling in the equipment training program.
Some of the thin film metal deposition in this work is performed on the sputtering deposition subsystem on “PVD1” tool at the 4D Lab Nanofabrication and Nanoimaging Facility. Sputtering deposition provides relatively more conformal surface coating than thermal deposition. For processes that require more reliable step coverage, sputtering coating is preferred.

Two exemplar deposition recipes are given below:

**Cr 5 nm Deposition (on PVD1 DC Sputter)**
- Ar flow at 100 % to $2 \times 10^{-3}$ mBar
- Pre sputter for 3 min at 35W
- Sputter for 2 min at 35W

**Ni 50 nm Deposition (on PVD5 DC Sputter)**
- Ar flow at 100 % to $2 \times 10^{-3}$ mBar
- Pre sputter for 5 min at 35W
- Sputter for 20 min at 35W

Detailed operating procedures can be found through the 4D Lab website or by enrolling in the equipment training program.
Spin Coater

Standard polymer resist spin coaters are available in the 4D Labs Cleanroom. The resist spin coaters are digitally programmable, able to accept more than three spin rate steps for each recipe.

Below is an example recipe for creating a 50 nm EBL writing layer using PMMA 2% (950M in Anisole):

1) Dispense sufficient resist liquid to cover approx. 90% of the substrate surface
2) Quickly activate spin coater at spin rates,
   • Step 1 – 500 rpm for 7 sec
   • Step 2 – 4000 rpm for 60 sec
   • Step 3 – 100 rpm for 10 sec
3) Remove sample for subsequent softbaking or other process steps

Reactive Ion Etch
The directional dry etching in this work is performed on the “RIE2” tool at the 4D Labs Cleanroom. This tool is equipped with five etching gas species: CHF$_3$, CF$_4$, SF$_6$, Ar, and O$_2$.

Some example recipes for etching are given below:

Borosilicate Glass using CHF$_3$/Ar
- CHF$_3$/Ar gas mixture at 30 and 4.5 sccm flows
- Set reactor pressure to 20 mTorr
- Energize plasma at 200 W
- Etching for 20 min yields rate of 3.4 nm/min

Fused Quartz using CF$_4$/O$_2$
- CF$_4$/O$_2$ gas mixture at 25 and 5 sccm flows
- Set reactor pressure to 10 mTorr
- Energize plasma at 200 W
- Etching for 10 min yields rate of 20 nm/min
Appendix B.

Additional Information on Key Processing Chemicals for Master Stamp Fabrication

Quartz Substrate Cleaning

Below is a list of the basic cleaning steps for quartz stamp substrates prior to further processing.

1) Sonicate substrate in acetone bath for 1 min
2) Sonicate substrate in IPA bath for 1 min
3) RCA-1 clean (no HF dip) for 10 min

Bath mixture

- 200 mL deionized-water [5 part]
- Heat water to 80 °C then add remaining parts according to order listed
- 40 mL NH4OH2 (29 %) [1 part]
- 40 mL H2O2 (30 %) [1 part]

4) Deionized-water rinse for 2 min
5) Nitrogen gas blow dry
6) Dehydration bake at 110 °C on hotplate for 2 min
A list of some common commercially available positive, negative, and chemically amplified EBL resists are given here:

Positive Tone Resists
- PMMA
- ZEP 520
- EBR 9
- PBS
- APEX-E *
- AZPF 514 *
- UV 3 *

Negative Tone Resists
- Ma-N 2400
- COP
- SAL 601 *
- NEB 22 *

* Indicates chemically amplified resist, with much lower sensitivity (requiring lower exposure dose) than conventional resists
PMMA processing and handling recommendations are given by most manufacturers of the chemical for micro/nanofabrication use.

Below is a summary of the common processing guidelines for the 950PMMA A resist (MicroChem Corp.) [92]:

**Spin Coating**
For static dispense, spread 5 – 8 mL for 150 mm wafer; or generally, dispense enough to cover 80 – 90 % of substrate surface.
Ramp to final spin speed at high acceleration and hold for minimum of 45 sec.
Typical thickness of film at final rate of 4000 rpm:
- 7% solid solution gives 380 nm
- 4% solid solution gives 200 nm
- 2% solid solution gives 60 nm

**Prebake**
For hot plate: at 180 °C for 60 – 90 sec
For convection oven: at 180 °C for 30 min
Typically the longer prebake the higher achievable resolution for EBL patterning on the resist, but also increases the sensitivity (exposure dose required) for the resist.

**Development**
Immersion is typically at room temperature (21 °C).
The most common developer mixture is MIBK with IPA at a ratio of 1 to 3 portions respectively; the resolution should be high, and the development time should be relatively longer than mixtures with less IPA, giving better control.

Immersion can be anywhere from 60 sec to 150 sec depending on prebake time and application needs.

**Postbake/Hardbake**
For hot plate: at 100 °C for 60 – 90 sec
For convection oven: at 95 °C for 30 min

**Removal**
Wet removal can be done with common cleanroom solvents such as acetone.
Specialty removers such as Microposit Remover 1165 may be more effective at elevated temperatures (e.g. 50 °C).
Sonication is necessary for faster removal.
Dry removal can be done with O₂ plasma or RIE.

**Chromium Etching, Wet Chemical**

Chromium is demonstrated in this work to be an effective pattern transfer layer material. Controlled Cr etch and pattern enlargement is a crucial aspect of the fast fabrication process. Here, a functional recipe and processing tips are given:

**Etchant**
- Use Transene AC1020 Cr etchant
• Diluted 1:1 with deionized water

Time
• Immerse for approximately 1 to 1:30 min
• Give light agitation every 15 sec
• Total immersion time depends on application and enlargement dimension desired

Stop bath & rinse
• Rinse under deionized water for a minimum of 2 min

Dry
• Blow dry with nitrogen gas

Au Etching, Wet Chemical

Gold is demonstrate in this work to be an effective lift-off layer material that is compatible with Cr as a pattern transfer layer. Wet etchants are commonly selective between Cr and Au. Here, the basic procedure commonly applied in this work to etch and undercut the Au lift-off layer is given:

Etchant
• Use Transene TFA Au etchant
• Diluted 1:20 with deionized water  (e.g. 5:100 mL)

Time
• Immerse for approximately 30 sec only (longer immersion may over etch most samples with nano-scale structures)
• Give light agitation every 5 sec
• Observe carefully to not over-etch, edges of features etch faster than center

Stop bath & rinse
• Rinse under deionized water for a minimum of 2 min

Dry
• Blow dry with nitrogen gas

The majority of the electroforming work is performed at the 4D Lab Nanofabrication and Nanoimaging Facility. Details of the operating procedures for the electroforming wet bench is available through the 4D Lab website or by enrolling in the equipment training program.

The basic composition and operating parameters of Ni sulphamate bath applied for most of the electroforming experiments in this work is given below:
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Per 1 L Bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfamate concentration</td>
<td>440 mL</td>
</tr>
<tr>
<td>Nickel bromide concentration</td>
<td>40 mL</td>
</tr>
<tr>
<td>Boric acid</td>
<td>30 g</td>
</tr>
<tr>
<td>Wetting agent HN-6 (mechanical agitation)</td>
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</tr>
<tr>
<td>Nickel sulfamate stress reducer additive</td>
<td>25 mL</td>
</tr>
<tr>
<td>Di water</td>
<td>To balance</td>
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</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Operating Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.6 – 4.2</td>
</tr>
<tr>
<td>Temperature</td>
<td>30 – 60 °C</td>
</tr>
</tbody>
</table>
Appendix C.

Basic Fabrication Process for PF-Based OLEDs

General Description

This section describes a simple process for fabricating a thin polymer film organic light-emitting-diode (OLED) on a flexible substrate. The OLED is based on a blue emitting semiconducting polymer poly(9,9-di-n-dodecylfluorene) (PDDF). PDDF is a polyfluorene (PF) family of light-emitting polymer often used in forming blue emitting OLEDs. The most of the OLEDs experimented in this work is a two-layer configuration; it includes a hole-transport layer; and, a light-emitting (a.k.a. emissive) active polymer layer.

The basic fabrication process is as follows [133]: First, a transparent conductive anode coated substrate is selected. Typically, indium-tin-oxide (ITO) is one of the few transparent anodes with the appropriate work function for OLEDs. In this work, commercially available ITO coated glass slides or polyethylene terephthalate (PET) films are used as substrate-anodes. A thin layer of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Sigma Aldrich) is spun onto the ITO coated substrates as the hole-transport layer. The PEDOT:PSS hole transport layer should be approx. 100 nm or less. Next, a PDDF solution (10 mg / mL in toluene) is prepared and spun onto the ITO coated substrates as the hole-transport layer. The PEDOT:PSS hole transport layer should be approx. 100 nm or less. Next, a PDDF solution (10 mg / mL in toluene) is prepared and spun onto the device to top of the PEDOT:PSS layer, forming an emissive layer in contact with the hole-transport layer. The emissive layer should be approx. 60nm or thicker. Although a spin-cast method is described here, it should be noted that with slight modifications to the solution, the functional polymers can also be sprayed or printed onto the appropriate substrates. Lastly, the cathode metal is applied on top of the emissive polymer. The cathodes can be deposited either by physical vapour deposition through thermal evaporation (e.g. Zn, Al, In), or by spray, print, or lamination (e.g. Ag ink, In foil, or liquid In:Ga). The work functions of the cathode must be appropriately matched to the emissive polymer.
The general device structure and the energy-level diagram associated to the functional polymers and metal contacts are illustrated below [133].

**Materials**

**OLED**
- Poly(9,9-di-n-ododecylfluorenyl-2,7-diyly), Sigma Aldrich 571652, 10 mg
- Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) conductive grade, Sigma Aldrich 483095, 1.3 wt% (soln in H₂O), approx. 6 mL
- Toluene (for making PDOF solution)
- Chloroform (for etching PEDOT-PSS and PDOF)

**Substrate/Anode**
- ITO coated PET (75 Ω/□ or better)

**Electrode/Cathode**
- PVD Zn, Al, or In
- In, In:Bi foil, or In:Ga liquid metal

**Tools**
Basic clean room polymer MEMS fabrication equipment (including hot plate, mask aligner, wafer spinner, sputterer, ultrasonic cleaner, air gun, oven, vacuum oven wafer tweezers, wet bench, containers, measuring beakers, glass stirring rods, microscale, disposable small syringes, microfilters, etc.)

**Conductance of the Anode Metal Layer:**
Measure V/I, and calculate the sheet resistance, Rₛ, where:
\[
R_s = (\rho/t) = \frac{\pi/\ln2(V/I)}{t} = 4.53(V/I),
\]

The \(R_s\) for either the ITO layer on substrate should be targeted below 75 \(\Omega/cm\) for good results.

**Depositing the PEDOT-PSS Hole Transport Layer:**

The PEDOT-PSS solution may be shipped in a 500 mL bottle container or larger from the manufacturer. Transport this solution to a smaller container (e.g. 100 mL) for easier handling and use. Note that the PEDOT-PSS has special storage instructions. Read the MSDS before use.

Setup a small area lined with chemi-wipes on the spinner bench. Place the small bottle of PEDOT-PSS solution nearby on the bench. Extract the cleaned, dehydrated substrates that are ready to have active polymers deposited on top. Place and center the substrate on the spinner vacuum chuck. Turn on the spinner and set the spin-rate to 500 rpm to begin with, and the timer to 100 sec.

Obtain a clean 1 mL disposable syringe and a 0.45 \(\mu\)m syringe filter attachment. Without the filter attached, extract 1 mL of the PEDOT-PSS solution from the bottle and attach the filter on to the dispenser subsequently. Slowly push the solution through the filter and onto the slide carefully. Repeat the extraction (without filter attached) and dispensing (with filter attached) two more times. The total amount of solution dispensed should be roughly 2 mL to 3 mL. The solution should be distributed from the center of the slide outwards to cover as much surface of the slide as possible.

Spin the slide initially at 500 rpm for approximately 10 sec, then ramp up to 1000 rpm over the next 20 sec. Let the spinner finish spinning the remainder of the 100 sec. The spin rate can be slightly adjusted to achieve better coverage based on experience.

Any spills or droplets of the PEDOT-PSS solution on the countertop can be cleaned up using chemi-wipe and a small amount of water.

Upon completion of the spin, a thin even coat of PEDOT-PSS polymer should remain on the surface of the slide, resulting in a bluish-colour.

The disposable syringe and filter can be cleaned by repeated rinsing using DI-water, and saved for future use.

**Preparing and Depositing the PDDF Emissive Layer**

There may be pre-mixed solutions of the PDDF emissive polymer in toluene solvent at 10 mg / 1 mL polymer/solvent ratio. If such is the case, the solution should be checked to ensure there is no excessive evaporation of the solvent, and that the solution is quite “liquidy”.

*Approximately 1 mL of the mixed solution will be required.*

*If no pre-mixed solution is available, the solution can be prepared.*

*To prepare the solution, preheat a small hotplate to approximately 50 °C. This hotplate should be under a fume hood. If there is no temperature indicator, a small beaker filled with after with a thermometer placed inside can be used to monitor the rise in temperature.*
While the hotplate is preheating, obtain a cleaned small beaker (50 mL). Place this beaker on a microscale and tare it to read zero on the digital display. The microscale should have at least ± 2mg resolution. Carefully extract and measure 100 mg of the PDDF polymer (whitish powder form) using a micro-scapula. Note that the PDDF also has special storage instructions also. The MSDS should be reviewed prior to working with this material.

Under the fume hood, using a cleaned 10 mL graduated cylinder, measure 10 mL of toluene. If the solvent is kept in a large heavy container, a small amount can be poured out into a small beaker first, for easier handling.

Mix the 10 mL toluene into the small glass beaker containing the PDDF gradually while stirring with a glass stirring rod. Place the beaker onto the hotplate at 50 °C and continue stirring. The polymer should dissolve quickly. Stir constantly for a total of 15 min while removing the beaker periodically from the hotplate if bubbling occurs (indicating evaporation of solvent). Let the solution cool on the hotplate for another 15 min, then remove from hotplate and let cool for 20 min. The solution is ready for dispensing.

Setup a small area lined with chemi-wipes on the spinner bench. Obtain a clean 1 mL disposable syringe (separate from the one used for PEDOT-PSS). Place the dehydrated PEDOT-PSS slide on the spinner vacuum, and center the slide. Adjust the timer again to 100sec and spin rate to 500 rpm.

Extract 0.5 mL of the solution using the fresh syringe and dispense the solution from the center of the slide outward, covering as much of the slide as possible. Begin the spin at 500 rpm for approximately 10 sec before ramping gradually up to 2000 rpm over the next 20sec and then letting the spin complete at this rate for the remainder of the 100 sec.

Upon completion of the spin, a thin even coat of PDOF polymer should remain on the surface of the slide. The PDOF layer has a yellowish colour.

Once the spin is complete, place the slide in the 100 °C oven to bake for a minimum of 15 min. Repeat for the second slide.

As before, the disposable syringe and filter can be cleaned by repeated rinsing using DI-water, and saved for future use, but ensure that it is designated only for PDDF to avoid cross contamination.