ADVANCED NANOIMPRINT PATTERNING
FOR FUNCTIONAL ELECTRONICS
AND BIOCHEMICAL SENSING

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Abstract

Nano-fabrication has been widely used for a variety of disciplines, including electronics, material science, nano-optics, and nano-biotechnology. This dissertation focuses on nanoimprint lithography (NIL) based novel nano-patterning techniques for fabricating functional structures, and discusses their applications in advanced electronics and high-sensitivity molecular sensing.

In this dissertation, examples of using nano-fabricated structures for promising electronic applications are presented. For instance, 10 nm and 18 nm features are NIL-fabricated for Si/SiGe heterojunction tunneling transistors and graphene nano-ribbon transistors, using shadow evaporation and line-width shrinking techniques, respectively. An ultrafast laser melting based method is applied on flexible plastic substrates to correct defects of nano-features. Nano-texturing of sapphire substrate is developed to improve the light extraction of GaN light emitting diodes (LEDs) by 70 %. A novel multi-layer nano-patterned Si-mediated catalyst is discovered to grow straight and uniform Si nanowires with optimized properties in size, location, and crystallization on amorphous SiO₂ substrate.

Nano-structures are also functionalized into highly sensitive bio-chemical sensors. Plasmonic nano-bar antenna arrays are demonstrated to effectively sense infrared molecules >10 times better than conventional plasmonic sensors. As small as 20 nm wide nano-channel fluidic devices are developed to linearize and detect DNA molecules for potential DNA sequencing. An integrated fluidic system is built to incorporate plasmonic nano-structures for 30X-enhanced fluorescence detection of large DNA molecules.
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Chapter 1

Introduction

1.1. Nanopatterning and nanolithography

In the past 40 years, the rapid development of information technology has enabled an unprecedented fast exchange of information and accelerated the growth and advancement of many industries throughout the world. Inside our increasingly advanced laptops, smartphones, and motor vehicles, it is the billions of functional integrated circuits that ultimately play the indispensable role of weaving an invisible network that wraps up the whole globe. The continuous scaling down of feature size of complementary metal-oxide-semiconductor (MOS) circuitry 30% smaller every three years following Moore’s law [1], has been able to lower the cost, increase the device integration density, reduce the power consumption, and boost the speed of electronic devices. This trend is predicted by the International Technology Roadmap for Semiconductors (ITRS) to continue to at least the “22 nm node” (the width of equal line-space patterns) (Figure 1.1) [2].
As the dimensions of electronic devices/circuits have been shrunk to nano-meter scale, conventional photolithography has been stretched to its limit to use shorter-wavelength light (now prevalently 193 nm). Some resolution-enhancing techniques, including immersion lithography [3], double patterning [4], and others (e.g. phase shifting masks [5] and optical proximity corrections [6]), have been used to reduce the feature size to the 32 nm node [2, 7]. However, as nano-lithographical tools become more expensive and the lithographical requirements more stringent, new nano-patterning techniques are necessary for both industrial and research applications [8].

One way to achieve ultra-fine nano-scale features is to utilize other beam sources with smaller physical wavelengths, such as extreme ultraviolet (EUV) light ($\lambda \sim 13.5$ nm) [9, 10], X-ray beam ($\lambda \sim 5$ Å) [11, 12], electron beam (e-beam) [13, 14], focused ion beam (FIB) [15-17], and most recently developed Helium ion beam [18]. Among them, EUV
lithography has already been adopted to the current 32 nm node [7], but its applicability is restrained by the unavailability of high-power EUV sources, the complexity and high cost of high-quality EUV masks, the low-sensitivity and low-resolution of the EUV resists, and complex and expensive optical systems [8, 10]. X-ray lithography faces similar challenges to a greater extent [8, 12], as it operates at a similar but shorter wavelength. Comparatively, e-beam lithography, FIB lithography, and Helium ion lithography could achieve sub-10 nm solution [13] by controlling the scanning beam, but they require serial writing, and thus are not compatible with high-throughput and low-cost industrial requirements. Therefore, they are more widely used in laboratories for research purposes and prototype demonstrations.

Instead of using radiative beam sources for nano-patterning, an alternative approach is to use either physical masking and printing or chemical assembly and modification. Sometimes named as unconventional lithography, this category includes dip-pen lithography [19, 20], soft lithography [21, 22] (including micro-contact printing [23], replica molding [24], molding in capillaries [25], transfer-printing [26]), ink-jet printing [27, 28], nanosphere lithography [29], anodic aluminum oxide (AAO) lithography [30, 31], nano-stencil lithography [32], self-assembly of diblock copolymers [33-36], DNA self-assembly guided lithography [37, 38], and last but not least, nanoimprint lithography (NIL) [39-41].

The advantages of these approaches include [8]: (1) no optical diffraction limit for resolution; (2) potential compatibility with unconventional substrates, such as plastics; (3) inexpensive patterning without requiring sophisticated optical alignment or radiation
sources; (4) capability of direct patterning of 3D functional structures without intermediate resist.

However, not all of the above methods are ideal for all applications. For example, dip-pen lithography is a tip-based, relatively slow, serial process, and could find most of its applications in chemistry. Soft lithography has been widely used for various applications especially in biochemistry [42, 43] because of its high throughput, low cost, and compatibility with multiple materials/substrates, but the soft and flexible feature of the stamp made in Polydimethylsiloxane (PDMS) makes it hard to bring the resolution below sub 30-50 nm [22]. Nanosphere lithography, AAO lithography, and nano-stencil lithography all rely on physical masks/templates for the nano-patterning, but the masks/templates generally can not be reused (nanosphere and AAO) or have to be regularly cleaned (nano-stencil), making the patterning process complicated and not reproducible (new mask every time). Self-assembly of block copolymers and DNA molecules can provide a route to ultra-small features, e.g. 20 nm pitch [44], but stringent control of experimental parameters is demanded for the formation of large-area ordered patterns (especially for DNA assembly) and some times e-beam pre-patterning is necessary to achieve better uniformity and addressable control.

Different from these approaches, Nanoimprint lithography has the advantages of high throughput (parallel patterning), high resolution (sub 10 nm), and low cost, and therefore is viewed as a viable candidate for next-generation nano-patterning on the ITRS roadmap [2].
1.2. Nanoimprint lithography for nano-scale structures and devices

Nanoimprint lithography (NIL) [39-41], proposed and demonstrated by Prof. Stephen Y. Chou in 1995, uses mechanical deformation to transfer topographic patterns from a mold, which is typically made in a rigid material such as Si or SiO$_2$ but could be softer materials such as PDMS, into an intermediate material, such as polymers and amorphous metals [45], and further down to a substrate by etching or a liftoff technique (Figure 1.2). The final substrate has either a complementary or identical pattern to the master mold, and can be either processed to functional structures and devices or treated as a daughter mold, which hence greatly extends the lifetime of the master mold and reduces the cost of the NIL process.

Figure 1.2 Key steps of nanoimprint lithography: (a) imprint resist coated on substrate; (b) imprint with a mold to deform resist to create a height contrast; (c) mold removed; (d) pattern transfer after etching residual resist.
With an extraordinarily high resolution of sub 10 nm [41, 46] (Figure 1.3) well beyond the capability of conventional photolithography, a high throughput (within one minute per wafer), a wafer-scale uniformity using air-cushion technique [47], and sub 20 nm alignment capability using Moire patterns [48], NIL has been adopted as one of the most important research tools in nano-patterning throughout the world (>30 countries/territories according to ISI Web of Knowledge database).

Due to its great advantages compared to other lithographical technologies, NIL has been widely used in different disciplines to study the novel phenomena of nano-scale devices. Previously Prof. Chou’s Nanostructure lab has already demonstrated many of them (Figure 1.4), including electronic devices such as room-temperature single-electron transistors [49], quantized magnetic disks [50], and 60-nm transistors [51], nano-optical devices such as infrared nano-rings resonators [52], solar blind UV (250-350 nm) filters [53], and plasmonic antenna arrays [54], and bio-nanofluidic devices such as fluidic nano-channels for DNA analysis [55-57], bumper array for biomaterials manipulation [58], and nano-gap detector for DNA sequencing [59], just to name a few. The different
formats of NIL, e.g. roller nanoimprint (or roll-to-roll, R2RNIL) [60, 61] and step and flash nanoimprint (SFIL) [62], have extended the NIL capabilities to large-area inexpensive patterning and high-speed industrial applications.

Figure 1.4 Selected applications by nanoimprint lithography: (a) a room-temperature single-electron transistor [49]; (b) a 60-nm transistor on 4-in. wafer [51]; (c) infrared ring-resonators (1 μm pitch, 500 nm diameter, and 15- and 35-nm high Au) [52]; (d) plasmonic antenna arrays (200 nm pitch, Au on SiO₂ pillars) for ultra-sensitive sensing [54]; (e) nano-fluidic channels for DNA stretching [55]; (f) a nano-gap detector in nano-channel for DNA sequencing [59].
1.3. Dissertation structure

In this dissertation, various NIL nanopatterning techniques for creating small, uniform, and functional nano-features over a large area without EBL writing will be discussed first, and then applications of NIL in electronics, surface material physics, nano-photonics, and nano-biofluidics will be presented along with corresponding nano-feature fabricating techniques (Figure 1.5).

Specifically, chapter 2 reviews detailed approaches of fabricating nanoimprint mold with various nano-features, including gratings (down to ~35 nm for 200 nm pitch, and 100 nm for 5 µm pitch), holes, and pillars (from >100 nm to sub 30 nm). Chapter 3 discusses a nano-feature improving technique, namely self-perfection by liquefaction (SPEL), with the focus on its applications on plastic substrates. Chapter 4 summarizes the fabrication of sub 10 nm asymmetric trenches and sub 20 nm channels and ribbons for potential electronic applications such as hetero-junction tunneling transistors and graphene devices. Chapter 5 studies the controlled uniform growth of Si nanowires on an amorphous SiO₂ substrate using a new nano-patterned host-mediated catalyst. Chapter 6 demonstrates the fabrication and performance enhancement of nano-patterned
GaN/sapphire light emitting diode (LED) devices. Chapter 7 introduces a new fabrication method of plasmonic nano-bar structures and its application in high-sensitivity infrared molecule detection. Chapter 8 focuses on nano-channel fluidic devices for DNA stretching and analysis. Chapter 9 includes a novel approach to integrate plasmonic structures into fluidic system for enhanced detection of DNA molecules labeled with fluorescence dyes. Finally, chapter 10 concludes the dissertation with the opportunities of future studies.
Chapter 2

Nano-pattern Generation Techniques Using Nanoimprint Lithography

2.1 Introduction

In a typical nanoimprint lithography (NIL) process, four components are indispensable: the imprint machine, the substrate, the imprint resist, and the mold. The machine and the substrates (typically Si, SiO₂ or sapphire wafers, or plastic substrates) are commercially available and thus outside the scope of this dissertation. In this chapter, the focus will be on some fundamental techniques to create desired nano-scale ultra-fine patterns over a wafer scale for imprint molds without using e-beam writing, with discussions on imprint resist also included.

2.2 Nanopatterning by nanoimprint lithography

As discussed in previous chapter, NIL has an ultrafine patterning resolution, especially when using rigid materials as the mold which are free from deformation in imprint, making it feasible to press and transfer the ultra-small features into the resist. However, the pattern has to be transferred to the underlying substrate, unless the resist
itself is the desired functional material. Therefore, etching of resist and substrate is necessary to conclude the NIL process. Although in principle both dry etching (typically reactive ion-etching, or RIE) and wet etching can be used, RIE is more popular for its better resolution and etching uniformity over wafer size.

To transfer the patterns to the substrate, there are two basic approaches (Figure 2.1): direct etching using the resist as the mask (Figure 2.1 b-c), or etching using a complementary hard mask (typically metal, e.g. Cr) patterned by a lift-off technique (meaning the resist is dissolved so that only the initial resist-free area has the hard mask) (Figure 2.1 d-g).

![Figure 2.1 Two approaches for pattern transfer to substrate in nanoimprint lithography. (a) Imprinted resist on a substrate. b-c, Direct etching approach: (b) substrate etching, and (c) resist removal. d-g, Liftoff approach: (d) evaporation of metal (Cr), (e) Cr liftoff, (f) RIE with Cr mask, and (g) Cr etch.](image-url)
There are several issues to be considered before designing a NIL process, including the mold material, the imprint resist, imprint parameters (pressure, temperature, etc.), and also the desired feature topography.

For a NIL mold, as discussed in chapter 1, essentially many materials can be used [63], but in this dissertation thermally grown SiO₂ is typically chosen for the following reasons: (1) Si wafers are widely available, and the film growth techniques of SiO₂ are highly reproducible; (2) SiO₂ (and Si) is physically rigid and chemically stable, i.e. free from swelling (e.g. with water), deformation, or breaking, and thus is suitable for a high resolution nanoimprint and a long mold lifetime; (3) the etching of SiO₂ has been well studied [64-67], and a CF₄/H₂ based RIE [66-68] can simultaneously achieve fast etching rate (~55 nm/min), steep side-wall (~85°), and good selectivity over Si (typically >3:1), very desirable for high-throughput and high-resolution patterning; (4) the SiO₂ surface is naturally terminated with silanol groups (~SiOH) [69, 70] and ready for chemical self-assembly of a fluorosilane-like mold release agent (MRA, Nanonex NXT-110) for easy mold separation.

It is often convenient to choose the SiO₂ thickness close to the desired feature height, so that the Si substrate can be used as an etch-stop layer due to the high etching selectivity. A slight over-etch can thus be used to ensure good feature height uniformity and straight sidewall (especially at the feature foot) over a whole wafer. The feature height and hence the SiO₂ thickness can range from sub-50 nm to 200 nm or even larger, determined by the feature aspect ratio, i.e. the height over the lateral size, which is typically >1 and preferably 2-4 for high-fidelity transfer of sub-100 nm features.
Table 2.1 Comparisons of two fundamental NIL methods: thermal NIL and UV NIL.

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<th>Imprint method</th>
<th>Thermal NIL</th>
<th>UV NIL</th>
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<td><img src="image2" alt="UV NIL Schematic" /></td>
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<td><strong>Resist</strong></td>
<td>Thermoplastic polymers, such as: 1. Nanonex NXR-1025 2. PMMA (higher temperature and higher pressure required)</td>
<td>Double layer polymers: 1. top UV-curable low-viscosity monomer (Si-containing NXR-2030, Si-free NX-2110) 2. transfer sub-layer (NXR-3022 and NXR-3032)</td>
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The NIL process can be categorized into two fundamental approaches (Table 2.1), thermal NIL (T-NIL) and photo-curable NIL (UV-NIL, since UV light is most commonly used). T-NIL uses a thermoplastic resist (e.g. Nanonex NXR-1025, also called NP69),
which is solid at room temperature but becomes viscous liquid when heated above its glass transition temperature ($T_g$). The resist is pressed together with the mold and heated above $T_g$, and thus deformed to a complementary pattern, which is retained during cooling and mold separation. NXR-1025 is used in this dissertation, rather than PMMA as it has a lower $T_g$ (~60°C) so that lower temperature and pressure can be used for high-fidelity imprint and a prolonged mold lifetime. Differently, UV NIL uses a UV-curable monomer or initiator (e.g. Nanonex NXR-2030, also called PUV30), which is a low-viscosity liquid as-spun but cross-links to solid when UV-exposed. Typically, the cross-linked UV resist does not readily dissolve in organic solvents, so that an underlayer (e.g. Nanonex NXR-3022, also named SUB2) is used in a combination to better remove the UV resists.

To find the best NIL process for desired applications, it is necessary to understand the advantages and drawbacks of the two NIL processes and the imprint resists associated with them.

The T-NIL process is simple and straightforward, as only a single-layer resist is needed for imprint, a single step O$_2$ plasma etching is required to remove the residual layer, and a solvent (e.g. acetone) rinse and spray works well for liftoff. The process is thus less equipment-demanding and potentially cheaper.

However, there are also some drawbacks of T-NIL: (1) the process requires heating, and thus is not compatible with many applications on low-$T_g$ plastic substrate; (2) it is relatively slower compared to UV-NIL (but still <5 min per wafer using Nanonex NX 2000 series imprinter) as heating and cooling both require ~1 min, limiting its use in some high-throughput industrial applications; (3) the resist may gradually soften after
imprint and thus sharp features may get distorted during long-time storage; (4) the heating/cooling may cause slight feature expansion or shrinkage and affect the resolution; (5) the thermoplastic resist is not robust when exposed to high-energy ion bombardment and can seriously deform or collapse, making it non-ideal for direct substrate etching. Therefore, T-NIL is typically good for liftoff of regular grating/trench and pillar patterns.

In T-NIL, oxygen etching also attacks the resist laterally to make the resist slope less steep and cause feature size variation, and hence reduces the resolution. The solutions to this may include: using a high aspect-ratio steep-sidewall mold for imprint, minimizing the residual layer thickness and the etching time, and capping the resist top with hard metal mask (e.g. Cr) by shadow evaporation [71, 72]. The shadow evaporation (typically bi-directional for 1D gratings/trenches and four-directional for 2D holes/pillars) caps the resist with a thin Cr mask by depositing from an oblique angle (typically 60~70° from substrate normal, 1-2 nm each direction). This technique is a great supplementary to T-NIL to avoid feature size distortion caused by lateral O₂ etching, enhance the resist feature aspect-ratio, steepen the resist side-wall, and facilitate a better liftoff. However, it requires multiple evaporations and is time-consuming. Some techniques for high-resolution transfer without shadow evaporations are discussed elsewhere (section 2.3.2).

In contrast to single-layer resist based process in T-NIL, UV NIL process typically uses a double layer, including a top low-viscosity Si-containing UV resist (NXR-2030) and a bottom water-soluble sub-layer (NXR-3022). This combination can eliminate the shadow-evaporation process, as the top UV resist can reliably mask the oxygen etching of the sub-layer and faithfully transfer the pattern to it. The process is free from heating, and thus in principle faster than T-NIL, compatible with inexpensive plastic substrates.
(Chapter 3), and potentially high-resolution as it is free of heating-caused feature
distortion. Besides, the UV resist can flow and fill readily due to its low viscosity, so that
a very thin residual layer (e.g. close to 0 nm, section 2.5) can be achieved. This can hence
minimize the etching-related feature size variation and benefits fine feature transfer.
Moreover, the UV resist and under-layer are both resistant to high-energy ion
bombardment so that they work well to mask direct substrate etching (Chapter 8).
Therefore, UV NIL is ideal for high-resolution, low-temperature, low-pressure, and high-
throughput patterning, for imprint of complex structures such as rings, triangles, and non-
flat surfaces for which shadow evaporation is not suitable, and for direct substrate etching
and reversing the mold patterns (e.g. from pillars to holes or vice versa).

UV-NIL, however, also has its limitations: (1) either the mold or the substrate has to
be a UV-transparent material such as fused silica, sapphire, etc., potentially raising the
cost; (2) carefully testing may be necessary to optimize the etching recipe; (3) the UV
resist is light-sensitive and should be stored in dark to avoid degradation; (4) the Si-
containing UV resist can be very difficult to remove once cured, so that caution should be
taken to avoid mold contamination (an alternative choice would be to use Si-free UV
resist NXR-2110).

Therefore, many factors, including feature size, feature shape, imprint resist
properties, imprint parameter requirements, cost, etc., should be considered before one
decides what NIL process should be used for the specific applications.

2.3 Fabrication of one-dimensional grating mold

In NIL, the simplest and most basic structures are one-dimensional gratings, from
which more complex structures (such as two-dimensional holes, pillars, bars, etc.) can be
generated by crossing two or more layers of gratings [50, 73] on a wafer-scale without any e-beam writing. In this section, the general methods of fabricating and manipulating grating molds are discussed.

2.3.1 Master grating mold fabrication

The master grating mold (in contrast to the duplicated molds which are called daughter molds) can be made in many methods, such as photolithography, e-beam lithography, interference lithography [74], copolymer self-assembly [44], and others. Among these approaches, interference lithography is used in our lab for its large-area, uniform, and nano-scale patterning capabilities [68, 73]. By changing the light source wavelength and the incidence angle, the grating pitch can be flexibly tuned, e.g. from 190 nm (using a 351 nm laser) to 1 μm or larger [68, 73]. The exposed resist pattern can be transferred to SiO₂ or Si gratings using feature-improving techniques, such as: (1) feature aspect-ratio enhancement by either a bi-directional shadow-evaporation or a tri-layer resist stack with a bottom anti-reflection coating (or ARC), a dielectric coating, and a top photoresist layer [68], and (2) smoothing the grating sidewalls using an anisotropic Si etching [72].

2.3.2 Fabrication of a grating mold with reduced width (sub 35 nm)

The grating molds fabricated by interference lithography typically have a close to 50% duty cycle (the ratio of protrusive part to the pitch), meaning the line-width is about 100 nm for 200 nm pitch grating. Variable grating widths, especially from 100 nm to sub 20 nm, can be useful for many nano-scale device applications. Some techniques such as shadow-evaporation can be used to slightly tune the line-width, but not aggressively, as
thicker metal deposition can cause line-edge roughness problems and degrade the grating quality. Here we discuss a new method of line-width shrinking to achieve 35 nm features over wafer scale (4”). The fabricated mold can work as a master mold to fabricate gratings narrower than 20 nm (Chapter 4).

Figure 2.2 Fabrication schematics of narrow nano-grating mold using a tri-layer structure (imprint resist/SiO2/ARC): (a) SiO2/Si substrate cleaning, (b) tri-layer deposition on SiO2/Si, (c) imprint with a grating mold, (d) oxygen RIE to remove residual layer and also trim the line with, (e) RIE to transfer pattern to SiO2 gratings, (f) RIE to pattern ARC, (g) RIE to pattern SiO2 substrate, (h) ARC removal and mold cleaning.
In this feature-size trimming technique, the use of a tri-layer imprint resist structure was very important. The tri-layer includes a top-layer of thermoplastic imprint resist (NXR-1025, Nanonex Corp.), a middle-layer of 10-20 nm e-beam evaporated SiO₂, and an under-layer of ARC (Antireflection coating XHRiC-16, Brewer Science, Inc.) (baked at 180 °C for 30 min to crosslink). After imprint, the features in the thermoplastic resist were narrowed by oxygen plasma, and then transferred down to the SiO₂ and ARC layers (Figure 2.2 b-f), which masked the mold etching in thermally grown SiO₂ (Figure 2.2 g).

This tri-layer structure is advantageous, because of its compatibility with various lithography approaches (cross-linked ARC is chemically inert in solvents/resists), high etching selectivity to Si or SiO₂ substrate, easily tunable feature aspect-ratio (e.g. by changing the ARC thickness), and convenient resist removal (by standard cleaning RCA). By combining with NIL, it further provides flexible and controllable line-width shrinking (by oxygen etching), multi-functionality as either a positive-tone (ARC liftoff) or negative-tone resist (direct etching), high-fidelity pattern-transfer, and a large-area patterning uniformity (based on dry etching, with variation <1 % [75, 76]).

To get a sub-35 nm wide grating mold, 130 nm thermally grown silicon oxide was RCA-1 (NH₃H₂O:H₂O₂:deionized water = 1:1:5, 80 °C) cleaned and used as the substrate, and a master grating mold (120 nm wide, 200 nm pitch) was used for imprint (250 PSI, 130 °C, 5 min, Nanonex NX 2000 imprinter). The as-imprinted tri-layer consisted of ~150 nm high, ~80 nm wide grating in thermoplastic imprint resist with ~65 nm residual layer, ~20 nm evaporated SiO₂ and ~160 nm ARC, as shown in the scanning electron microscope (SEM) image Figure 2.3a.
Figure 2.3 Cross-sectional SEM images of fabrication steps to make a 35 nm wide grating mold: (a) As-imprinted 80 nm wide gratings in tri-layer structure (imprint resist/SiO$_2$/ARC) on thermal SiO$_2$. (b) Oxygen-plasma shrunk 40 nm wide resist gratings. (c) O$_2$/CHF$_3$ RIE patterned 40 nm wide SiO$_2$ mid-layer. (d) Oxygen RIE transferred 35 nm wide ARC gratings. (e) CF$_4$/H$_2$ RIE defined 35 nm gratings in thermal SiO$_2$. (f) Final 35 nm wide grating mold after RCA1 cleaning. Scale bars are all 200 nm.

Then, a high-pressure O$_2$ plasma etching (10 sccm, 50 W, 50 mtorr, 2 min 30 sec) reduced the top-layer resist grating width to ~40 nm, while removing the residual resist in the trench (Figure 2.3 b). An O$_2$/CHF$_3$ RIE (1.5/10 sccm, 100 W, 2 mtorr, 2min 30 sec)
etched through the 20 nm SiO₂ mid-layer masked by the top resist grating (Figure 2.3 c). Another oxygen RIE (10 sccm, 50 W, 2 mtorr, 6 min) patterned the bottom layer resist (i.e. ARC) into 160 nm high 35 nm wide gratings (Figure 2.3 d), laterally undercutting ARC by 5 nm. The triple layer resist pattern was used as a mask in etching 35 nm wide 130 nm deep gratings in the SiO₂ mold using CF₄/H₂ RIE (33/7 sccm, 300 W, 50 mtorr, 3 min) (Figure 2.3 e), with 30% overetch to obtain vertical SiO₂ grating sidewalls and flat Si bottom surfaces. Here the Si wafer acted as an etching-stop material due to its low etching rate in CF₄/H₂ [77]. Finally, a 15 min RCA-1 cleaning stripped off the triple-layer resist (Figure 2.3 f), and the mold was vapor-treated with anti-sticking mold-release agent (NXT-110, Nanonex Corp., 110°C, 30 min).

![Figure 2.4 Imprinted nano-trenches in resist with 35 nm wide grating mold: (a) cross-sectional view; (b) top-view.](image)

Using the fabricated narrow grating mold, resist (NXR-1025) was patterned into 35 ± 2 nm wide narrow trenches by NIL (130°C, 150 PSI, 3 min). The resist trenches were much narrower than the original imprinted trench (120 nm) (Figure 2.3 a), with a thin residual layer of ~5 nm (Figure 2.4 a) and good uniformity (Figure 2.4 b).
2.4 Fabrication of two-dimensional nano-holes by NIL

Two-dimensional nano-hole structures can provide more interesting functionalities than one-dimensional gratings, particularly in nano-optics [53, 78, 79]. To fabricate such a hole mold, one can use double nanoimprint lithography to create nano-holes in a Cr mask from two orthogonal sets of metal gratings, and transfer the pattern into the substrate by RIE (Figure 2.5). Specifically in the fabrication, 85 ± 2 nm square holes were created by crossing two Cr masks (15 nm thick each) and using CF$_4$/H$_2$ RIE to etch 130 nm deep in SiO$_2$ (Figure 2.6 a). The imprinted patterns in resist using the fabricated hole mold were complementary nano-pillars of 85 ± 3 nm wide and 130 nm high with a good uniformity over 4” wafer (Figure 2.6 b-d).

Figure 2.5 Schematics of fabrication process for 2D nano-hole structures: (a) SiO$_2$/Si substrate; (b) 1$^{st}$ grating set imprinted in resist on SiO$_2$/Si; (c) residual layer etching; (d) 1$^{st}$ Cr grating liftoff; (e) 2$^{nd}$ Cr grating liftoff; (f) SiO$_2$ RIE and Cr removal.
Figure 2.6 Fabricated nano-hole mold and the corresponding imprinted patterns in resist: 
(a) nano-holes in SiO$_2$ with Cr mask; b-d, imprinted nano-pillars in resist: (b) top-view, (c) large-area top-view, (d) cross-sectional view.

2.5 Fabrication of 2D nano-pillars by NIL

Two dimensional nano-pillar structures also have many important applications, both in electronics [50] and optics [54]. Similar to nano-holes, nano-pillars can also be patterned over a wafer scale by NIL without using e-beam writing. In this section, several approaches of fabricating of pillar structures (imprint molds) are presented.
2.5.1 Fabrication of nano-pillars by double NIL

Nano-pillars can be created by orthogonal double nano-imprint and etching, similar to the approach for nano-hole fabrication (section 2.4). To create pillars rather than holes, the second NIL was performed not on Cr lines but on bare SiO₂ gratings without Cr (Figure 2.7). For mold protection and easy resist filling, the resist in 2\textsuperscript{nd} imprint was thicker (~280 nm) than that for the first (140 nm). A Cr bi-directional shadow evaporation capped the 2\textsuperscript{nd} resist gratings, and oxygen RIE completely removed the residual layer. The 2\textsuperscript{nd} liftoff then deposited Cr both on top of SiO₂ gratings and in the
trench (Figure 2.7 f). The following CF$_4$/H$_2$ based RIE etched the SiO$_2$ gratings not covered by Cr mask, hence creating the square pillars in the regions overlapped by SiO$_2$ and Cr grating masks patterned in the two sets of NIL (Figure 2.7 h). The reasonably high etching selectivity of SiO$_2$ to Si by CF$_4$/H$_2$ RIE ensures high-fidelity pillar patterning with minimal height difference caused by Si etching (30-40 nm) (Figure 2.8 a-b).

![Figure 2.8 SEM images of 115 nm pillar mold for nano-pattern transfer: (a) fabricated mold with 115 nm sized pillars; (b) UV imprinted patterns in resist; (c) residual layer etching; (d) Cr squares liftoff.](image)

The fabricated pillar mold (with 115 ± 3 nm sized pillars, Figure 2.8 a) can be used for pattern transfer by either T-NIL or UV-NIL, but UV-NIL (Figure 2.8 b) may have more advantages: (1) the non-flat imprinted pattern is not convenient for Cr shadow evaporation, so that the resist has to be etched without a metal mask to remove residual layer, which in T-NIL can lead to resist hole expansion and corresponding larger sized pillars after transfer; (2) a minimized residual layer (<5 nm, Figure 2.8 b) can be achieved...
in UV NIL for high-fidelity transfer (Figure 2.8 b). After UV-NIL, a 5s brief etching of top resist (NXR-2030, deposited ~150 nm thick, <5 nm residual layer after NIL) with O₂/CHF₃ (1.5/10 sccm, 100 W, 2 mtorr) and oxygen ashing (10 sccm, 50 W, 2 mtorr, 3 min) of bottom transfer layer (~130 nm thick NXR-3022) (Figure 2.8 c), the Cr square patterns can be transferred to a transparent fused silica substrate by liftoff with an equal size (115 ± 4 nm) as pillars on the mold (Figure 2.8 c).

2.5.2 Fabrication of nano-pillars using a tri-layer structure

![Figure 2.9 Fabrication schematics of a pillar mold by tri-layer structure based feature reduction:](image)

(a) SiO₂/Si substrate; (b) imprinted resist pillars on tri-layer; (c) resist pillar size reduction by oxygen plasma; (d) SiO₂ RIE; (e) ARC RIE; (f) thermal oxide RIE and cleaning.

The 2D pillars created by double NIL and etching (section 2.5.1) may have some issues in use, such as that the pattern top is non-flat and that the pillar size is not flexibly tunable (determined by the master grating width). One way to overcome these problems is to use a method based on a tri-layer structure (resist/SiO₂/ARC), similar to that
described in section 2.3.2 for shrinking 1D gratings. The key steps includes imprinting with a hole mold in the tri-layer, shrinking the patterns by oxygen etching, and further transferring the pattern to the substrate (Figure 2.9).

**Figure 2.10** SEM images of fabricating a 60 nm pillar mold using a tri-layer structure: a-b, imprinted resist pillars in tri-layer structure on SiO$_2$/Si substrate; c-d, pillar patterns transferred to SiO$_2$; e-f, pillar pattern transferred to ARC; g-h, pillars etched in SiO$_2$. 
The tri-layer was deposited on a RCA-1 cleaned 4” wafer with 130 nm silicon oxide, by spin-coating and baking 150 nm thick ARC at 180°C for 15 min, e-beam evaporating 20 nm SiO2, and coating ~85 nm thick thermoplastic resist (NXR-1025). Then a fabricated nano-hole mold (section 2.4) was used to create pillars in the resist by T-NIL (250 PSI, 130 ºC, 5 min), resulting in a residual layer of ~55 nm (Figure 2.10 a). Then an O2 plasma RIE (10 sccm, 50 W, 5 mtorr, 3 min) removed the residual resist and reduced the pillar size, O2/CHF3 RIE (1.5/10 sccm, 100 W, 2 mtorr, 2.5 min) etched through the SiO2 mid-layer, and another oxygen RIE (10 sccm, 50 W, 2 mtorr, 5 min) patterned the under-layer ARC into pillars (Figure 2.10 e-f). Finally, the ARC masked the etching of 130 nm thick SiO2 into pillars by CF4/H2 RIE (33/7 sccm, 300W, 50 mtorr), and the mold was cleaned in RCA-1 (Figure 2.10 g-h).

![Image of SEM images](image_url)

**Figure 2.11 SEM images of imprinting and duplication of 60 nm pillar mold: a-b, Top-view and cross-sectional views of imprinted 60 nm nano-holes in resist; c) nano-holes after etching residual resist; d) Cr dots after liftoff on Si substrate.**
This approach has two advantages: first, the oxygen plasma etching of resist can be easily tuned to achieve desired pillar size (60 nm); second, the fabricated pillar mold has a flat bottom surface.

Using the fabricated mold for T-NIL (~140 nm NXR-1025), a very thin (<25 nm) residual layer was achieved (Figure 2.11 a-b). A subsequent brief oxygen etching (10 sccm, 50 W, 2 mtorr, 1 min) was able to remove the residual layer (Figure 2.11 c), and Cr dots of the same size was reliably replicated after liftoff (Figure 2.11 d).

### 2.6 Fabrication of nano-pillars of arbitrary sizes and pitches by NIL

The previous sections discuss periodic nano-features of a very small pitch, i.e. 200 nm, with the master mold made by interference lithography. These nano-features can be used for many applications where high-density patterning [55-57] and/or sub-wavelength optical properties are desirable [52-54]. However, in some other applications, less dense nano-patterns are required for manipulation and characterization of each individual feature (grating, dot, hole, etc.). In this case, e-beam lithography is typically used for patterning, despite the long-writing time and non-reproducible feature sizes.

In this section, a NIL and edge-deposition based method is used to generate precisely controlled nano-features (gratings and pillars) with arbitrary periods (determined only by photolithography mask patterns, and demonstrated here as 5 μm) and duty cycles. This method, proposed by Prof. Stephen Y. Chou and demonstrated previously for fabrication of centimeter-long and sub 20 nm sized nano-channels [57], allows smooth feature definition, high-resolution, and fast and repeatable patterning.
2.6.1 Fabrication of nano-gratings of arbitrary sizes and pitches

Nano-grating fabrication consists of three key steps (Figure 2.12), Si layer thinning on a silicon-on-insulator (SOI) wafer, rectangular Si scaffold patterning, and Si$_3$N$_4$ grating definition. The grating patterns were created only at the edges of Si scaffold by combining conformal Si$_3$N$_4$ deposition and selective etching [57, 80].

The Si layer (Figure 2.12 a-b) was thinned by repetitive Si thermal oxidation (1000 °C, Tystar tube furnace) and SiO$_2$ stripping in diluted HF (1:50) from 2-3 μm to sub 100 nm. First the whole 4” (110) Si SOI wafers were wet oxidized to reduce the Si layer thickness to ~500 nm, and then diced into 1” squares, which were individually thinned by dry oxidation since the Si layer thickness was not uniform over 4” scale.

To pattern a smooth Si scaffold (Figure 2.12 c-g), 70 nm thick SiO$_2$ mask was deposited on 1” SOI squares by plasma enhanced chemical vapor deposition (PECVD) (Plasma-Therm 790, 2 % SiH$_4$ in N$_2$ at 35 sccm, N$_2$O at 160 sccm, 800 mtorr, 25 W, 250 °C), and then patterned into 20 mm long and 10 μm pitch stripes of 50 % duty cycle (equal stripe width and spacing) by photolithography (Karl Suss MA6 mask aligner) and RIE (Plasma-Therm 720, O$_2$/CHF$_3$ = 1.5/10 sccm, 5 mtorr; 100 W) (Figure 2.12 e). The SiO$_2$ stripes were aligned parallel to the Si (111) surface, and used to mask anisotropic KOH wet etching (20 % KOH, 13 % IPA, and 67 % DI water, temperature 60 °C) of the (110) Si layer, with the (111) Si sidewalls and buried oxide acting as etching-stop materials, to create smooth Si sidewalls and expose flat buried SiO$_2$ surfaces [81] (Figure 2.12 f). Finally the SiO$_2$ mask was stripped by floating the wafer face-down in diluted HF, which minimized the attack on the buried oxide layer (Figure 2.12 g).
Then Si$_3$N$_4$ gratings were then created at the Si scaffold edges by conformal deposition of ~85 nm Si$_3$N$_4$ by low-pressure chemical vapor deposition (LPCVD) (Tystar tube furnace, 50 sccm dichlorosilane, 150 sccm NH$_3$, 300 mtorr, 780 °C), anisotropic RIE etching of the Si$_3$N$_4$ covering the Si layer top surface and buried oxide layer (O$_2$/CHF$_3$ = 3/10 sccm, 15 mtorr; 100 W), and another anisotropic KOH etching to completely remove the top Si layer.

![Figure 2.12 Schematics of fabricating nano-gratings with controlled size and pitch. (a) A Si (110) SOI wafer; (b) SOI wafer with thinned Si layer; (c) PECVD deposition of SiO$_2$ on SOI; (d) Photolithography patterning photoresist gratings; (e) RIE patterning of PECVD SiO$_2$; (f) KOH etch of Si in unpatterned regions; (g) Stripping PECVD SiO$_2$ mask; (h) LPCVD conformal deposition of Si$_3$N$_4$; (i) RIE Si$_3$N$_4$ to expose Si; (j) KOH etch Si to form Si$_3$N$_4$ gratings.](image-url)
Due to the finite RIE etching selectivity of Si₃N₄ and SiO₂ (etching rate ratio ~2.3), a 20% overetch of Si₃N₄, which was necessary to expose the Si layer, also etched into buried oxide layer (Figure 2.12 (i)). This resulted in a slight height difference (~35 nm, Figure 2.13 (d)) on the two sides of the Si₃N₄ gratings, seen from the color difference in the optical image of the fabricated grating mold (Figure 2.13 (a)). From the thermally imprinted resist (NXR 1025) patterns (Figure 2.13 (b)), we can clearly see that the grating mold had a pitch of 5 µm, due to spatial frequency doubling from the original 10 µm pitch stripes [80], with a small pitch error (<5 %) due to well controlled duty-cycles of SiO₂ stripes during photolithography and RIE. The fabricated nano-gratings had smooth edges (due to KOH etching), a uniform width of 85 nm (determined by Si₃N₄ thickness), and a depth of ~80 nm (controlled by the Si layer thickness).

![Figure 2.13 Fabricated 5 µm pitch grating mold and imprinted patterns. (a) Optical image of fabricated SOI grating mold. b-d, SEM images of imprinted patterns in resist: (b) large-area top-view, (c) high-magnification top-view; (d) cross-sectional view.](image-url)
The imprinted patterns in ~130 nm thick resist (NXR-1025) (Figure 2.13 d) showed that the 5 μm pitch grating mold had slightly non-perfect geometries, such as non-leveled surfaces (due to overetch into buried oxide), non-flat grating top surfaces (trench bottom in resist, due to attack to SiN grating in RIE), and non-straight sidewalls. These issues do not seriously affect the use, but can be resolved through a mold duplication.

Figure 2.14 Duplication of 5 μm pitch grating mold. (a) Cross-sectional image of resist patterns after residual layer RIE. b-d, SEM images of duplicated gratings in 110 nm SiO₂: (b) large-area top view, (c) high-magnification side view; (d) high-magnification top view.

A 5 μm pitch, 90 nm wide, and 110 nm high grating mold was duplicated from the master SOI grating mold by thermal nanoimprint (NXR-1025 resist, 60 PSI, 130 °C), Cr bi-directional shadow evaporation, oxygen residual layer RIE (cross-sectional SEM Figure 2.14 a), 10 nm Cr liftoff, SiO₂ RIE (CF₄/H₂ = 33/7 sccm, 300W, 50 mtorr), Cr
etch, RCA1 clean, and mold treatment by MRA. The fabricated mold clearly has smooth grating lines of uniform width (~90 nm) (Figure 2.14 b-d).

2.6.2 Fabrication of 5 μm pitch nano-pillars/dots

![fabrication Diagram](image)

**Figure 2.15 Schematics of fabricating nano-pillars by crossing NIL gratings.** (a) A Si wafer with thermal SiO₂ layer; (b) NIL patterned resist using a grating mold; (c) Cr lines on SiO₂ after liftoff; (d) RIE patterned SiO₂ gratings on Si; (e) Cr dots on SiO₂ gratings after 2nd orthogonal NIL, residual layer RIE, Cr evaporation, and liftoff; (f) Nano-pillars on Si after RIE SiO₂ and Cr etch.
To fabricate the nano-pillars, a double NIL based method similar to the approach in section 2.5.1 was used to sequentially pattern two sets of orthogonal gratings, with the second one in resist and the first one in SiO₂, and select only the nano-dots overlapped by the two sets of gratings but etch away the rest (Figure 2.15).

Figure 2.16 SEM images of different steps in fabrication of 5 μm pitch pillars. (a) SiO₂ gratings on Si wafer; (b) Imprint 2nd gratings normal to SiO₂ gratings; (c) Cr dots lifted off on SiO₂ gratings; (d) SiO₂ dots after etching.

First, 130 nm thermal silicon oxide was patterned into gratings (SEM image in Figure 2.16 a) by T-NIL (130 nm thick NXR-1025 resist) using a daughter grating mold (90 nm wide, 110 nm high), Cr evaporation and liftoff, RIE (O₂/CHF₃ = 1/10 sccm, 5 mtorr; 200 W), and Cr etch (CR-7 etchant). Then another set of nano-trenches was imprinted in 2nd layer resist (~280 nm thick) orthogonal to the SiO₂ gratings (Figure 2.16 b), and capped
by Cr on the top by shadow evaporation. Following that, a carefully adjusted oxygen RIE partially removed the residual resist in the trenches to expose the top of SiO2 gratings, but left the Si substrate still resist-covered. Cr dots (10 nm thick) were then deposited by liftoff only on the SiO2 gratings but not on Si substrate surface (Figure 2.16 c). Finally, the Cr dots masked the etching (O2/CHF3 = 1/10 sccm, 5 mtorr; 200 W) of the SiO2 gratings into pillars (Figure 2.16 d).

In the fabrication, Cr dots, rather than Cr lines, were selectively deposited on SiO2 gratings and used to mask the etching of nano-pillars. This reduced the surface topological variation to only in one dimension rather than two dimensions, and allowed easier imprint resist filling in following pattern transfer, which is critical in applications where minimized residual resist thickness and high-fidelity pattern transfer is necessary.

In the SiO2 etching, an O2/CHF3 based chemistry and a moderate RF power (200 W) were used to achieve a high SiO2 etching rate (~19 nm/min), a high selectivity of SiO2 to Si (etching rate ratio ~4.3), and reduced substrate bombardment and thus minimized surface roughness. The etching depth into Si was minimal (~30 nm) when SiO2 not covered by Cr was fully etched away.

To transfer the nano-dot patterns, T-NIL (160 nm Nanonex NXR 1025, 60 PSI, 3 min, Figure 2.17 a-b) with the MRA treated nano-pillar mold, oxygen RIE (10 sccm, 50 W, 2 mtorr, 1 min, SLR 720), Cr evaporation (10 nm), and liftoff (Figure 2.17 c-d) were used. The Cr dots were 90 nm in diameter (Figure 2.17 d), slightly smaller than the original mold (Figure 2.16 d) and the imprinted hole size (Figure 2.17 b), because the non-vertical sidewall of the SiO2 nano-pillars (caused by moderate RIE power) effectively led to reduced pillar size.
Figure 2.17 SEM images of transferred patterns using the 5 μm pitch pillar mold. a-b, Imprinted 5 μm pitch nano-holes in resist: (a) a 4 by 4 array, (b) a high-magnification image of a single hole. c-d, Nano-Cr dots after liftoff: (c) a 4 by 4 array, (d) a high-magnification image of a single dot.

2.7 Summary

In this chapter, some fundamental NIL techniques were reviewed, and will serve as the foundation for understanding more complex patterning approaches and the corresponding applications in the following chapters.

NIL can be categorized into two widely used methods, i.e. T-NIL and UV-NIL, both of which are excellent for high-resolution patterning. Comparatively, T-NIL is simpler in
processing and preferable for fabricating regular structures such as gratings, pillars, and others. T-NIL can be combined with a shadow evaporation technique to achieve high-fidelity feature transfer. UV-NIL is more complicated but more applicable in complex structure patterning, offering good etching resistance and reliably masks substrate etching. The tri-layer technique is a RIE-based approach which can greatly enhance feature contrast (aspect ratio), boost etching resistance, and provide more flexibility in tuning feature size and shape, especially when combing with double nanoimprint technique (more examples discussed in chapter 8). Using nano-feature edges as the scaffold, NIL can pattern nano-gratings/trenches and nano-pillars/holes with a size of sub-100 nm, a feature pitch in micro-scale and arbitrarily tunable, and a good feature uniformity on a wafer scale. Based on the above approaches, uniform 1D gratings, 2D holes, and 2D pillars of desired dimensions were fabricated into wafer-scale imprint molds, and will be used for nano-feature patterning in the following chapters.
Chapter 3

Feature Optimization on Plastic Substrates through Self-Perfection by Liquefaction (SPEL)

3.1 Introduction

Plastic substrates are highly desirable for many future portable, flexible, inexpensive, and transparent electronics [82-84], such as displays [84], light emitting diodes (LEDs) [82], transistors [83, 85], and memories [86, 87]. To achieve high-throughput and high-resolution patterning, nanoimprint lithography (NIL) [88, 89] has been used on plastic substrates for electronic [90, 91] and optical [61] applications.

However, compared with hard solid substrates, plastic substrates have a number of problems in direct nanopatterning, such as low melting temperature [92], poor etching resistance [93], weak adhesion [94], and easy deformation (small elastic modulus [95]), all of which lead to poor patterning quality [96]. Therefore, generally nano-scale feature patterning on plastic substrate has much larger line-edge roughness, limiting the resolution and applications.
To reduce the feature roughness of nano-structures, one needs to either optimize the fabrication, including the mask (mold), the resist, the processing control (etching, evaporation, liftoff, etc.), or use post-fabrication improving techniques. Self-perfection by liquefaction (SPEL), demonstrated by Prof. Stephen Y. Chou and Dr. Qiangfei Xia, is such a post-fabrication technique which utilizes fast heating by an ultraviolet laser to melt and remove defects (Figure 3.1) [97]. The SPEL technique uses a 20-nanosecond pulsed excimer laser that heats only the surface layer of a structure and melts only the rough features in target areas, leaving the rest intact. Then the melted liquid structure (metal, Si, polymer, etc.) flows or is guided into desired smooth shapes. The SPEL process can be extended to use infrared heating to smoothen and fabricate 10 nm features [98, 99].
3.2 Nano-patterning on plastics by NIL and SPEL

Although SPEL has been used to optimize features on Si substrates, it has not been applied to plastics yet. In this section, a new method, which combines NIL and SPEL, is presented to achieve an array of round and smooth metal dots over a large area on plastic polyethylene terephthalate (PET) substrate with a high fidelity and high yield.

3.2.1 Fabrication process

The key novelties of our method are in the following three aspects.

(i) A thin (~450 nm) high melting-temperature (at least >1,100°C [100]) material, hydrogen silsesquioxane (HSQ), was used as the surface layer on top of the plastic PET, offering a good adhesion to both the PET and the metal (Cr) dots, a significantly enhanced etching resistance of the substrate, a stable and non-melting surface to Cr dots during SPEL, and an excellent heating protection (during SPEL) to the underneath PET substrate.

(ii) Nanoimprint lithography (NIL) [88, 89] and lift-off were used to pattern initial metal nano-structure array on PET over a large area.

(iii) SPEL [97] was used to reshape the initial non-circular metal patterns into dot arrays with a reduced lateral dimension (60 nm diameter) and perfectly round and smooth shape, which is difficult to achieve using other technologies.

Specifically, our approach has the following five detailed steps (Figure 3.2): (a) cleaning of a ~100 µm thick PET film (Melinex 454, Dupont Teijin Films) with methanol/isopropanol, followed by oxygen plasma at 50 W for 2 min to facilitate the subsequent HSQ coating; (b) spin-coating HSQ (Gelest, Inc.) on the PET, followed by baking at 110°C overnight in air ambient to drive off the solvent in HSQ film (to achieve
final thickness ~450 nm); (c) oxygen plasma treatment of the HSQ film at 50 W for 2 min, spin-coating double-layer UV imprint resist (NXR-2030 ~100 nm, NXR-3022 ~250 nm thick), and then UV NIL at 150 PSI and room temperature for 3 min with a fused silica mold (diced to ~30 × 30 mm²); (d) RIE residual imprint resist, and then e-beam evaporation and liftoff (spraying methanol/DI water with a 1:1 ratio) to pattern Cr dots; and (e) SPEL [97] using a 20 ns single pulse of 308 nm XeCl excimer laser to melt and reshape the Cr dots.

Figure 3.2 Schematics of fabrication of uniformly patterned metal-dot arrays on PET substrate using HSQ coating, NIL and SPEL. (a) A cleaned PET film. (b) Spin-coating of a thin layer of HSQ onto PET. (c) UV NIL with a pillar mold. (d) Evaporation of Cr metal and liftoff. (e) SPEL to perfect the Cr dots shape.
3.2.2 Nano-patterning in NIL resist on plastics

Figure 3.3 SEM images of large area NIL patterns on PET substrate: (a) a 235 nm pitch nano-pillar mold in SiO$_2$; (b) nano-holes in UV resist on PET.

Comparing the NIL mold (235 nm pitch, 106 ± 4 nm by 140 ± 3 nm, from Dr. Keith Morton) (Figure 3.3 a) and as-imprinted resist (235 nm pitch, 99 ± 4 nm by 136 ± 3 nm) (Figure 3.3 b), we can see that the large-area uniformity of the patterns was preserved during imprint. In the fabrication, the double-layer UV resist was used, because it not
only offers high resolution and low-temperature patterning, but also provides deep resist profile and easy dissolution of resist (under-layer is water soluble). Both of these features are key to a successful lift-off without using harsh resist removing methods (e.g. ultrasonic agitation or oxidative based resist remover) to avoid pattern distortion, substrate damage, and poor adhesion.

### 3.2.3 Challenges in patterning transfer on bare PET

To transfer the nano-features to the underlying substrate, the top resist residual layer was removed by $O_2/CHF_3$ plasma, and then the under-layer resist by $O_2$ plasma. For patterning on bare PET (without a HSQ layer), the fabrication of Cr dots had a very poor yield and bad control of the sizes, shapes, and locations. For example, an oxygen plasma could over-etch into the PET substrate, creating deep craters (Figure 3.4 a-b). PET has a poor etching resistance [93] and an etching rate (~20 nm/min) comparable to the NIL underlayer resist (~40 nm/min) under the same etching condition (50 W in Plasma-Therm SLR 720). Therefore, a slight 1-2 min over-etch of NIL resist, which was necessary for overcoming the non-uniformities in resist thickness and RIE etching rate while ensuring total removal of the resist, inevitably led to about 20-40 nm deep pits in PET. This resulted in the Cr dots patterned in the PET craters (Figure 3.4 a-b).

On the other hand, if there was no over-etch, the non-uniformities of the resist thickness (more significant on plastic due to the deformation) and RIE etching would leave resist residue in some of the etched holes, which would cause the Cr dots deposited inside these holes missing during the lift-off (Figure 3.4 c-d).
Moreover, the laser energy necessary to melt Cr in SPEL can also damage the PET film, evidenced by SPEL experiments with different energies: partial melting of Cr dots at 151 mJ/cm² (Figure 3.5 a-b) and complete melting at 168 mJ/cm² (Figure 3.5 c-d). Furthermore, due to surface energy difference (1.6 J/m² for Cr [101] and 60 mJ/m² for PET [102]), PET does not wet molten Cr. This made the molten Cr droplets move around on the PET surface to random locations, significantly destroying the periodicity of the array. Finally, the movement of the Cr droplets caused an agglomeration of several dots to form large-diameter, non-circular, and non-uniform dots (Figure 3.5).
Figure 3.5 SEM images and schematics of melted Cr dots with random locations and different diameters on bare PET after SPEL. a-b, partial Cr melting with SPEL at 151 mJ/cm²; c-d, complete Cr melting at 168 mJ/cm². Both samples were originally patterned as in Figure 3.4 a before SPEL.

3.2.4 Uniform nano-patterns on HSQ-coated PET

With a thin HSQ coating on PET, the poor patterning issues were all resolved. After liftoff, Cr nano-pads (100 ± 2 nm by 130 ± 3 nm, Figure 3.6 a) with a good fidelity (<7 % size difference from the pillar mold) were transferred on HSQ/PET over a large area (30 mm by 30 mm) (Figure 3.6 b). A single-pulse SPEL (168 mJ/cm²) successfully reshaped each Cr pad into a single dot with a nearly-perfect round hemisphere and also a significantly reduced diameter (87 ± 2 nm) (dot area on the substrate reduced by 55 %).
Figure 3.6 Cr dots array uniformly patterned on HSQ coated PET using NIL and SPEL. a-b, SEM images of NIL patterned Cr pads. c-d SEM images of round Cr dots reshaped by SPEL, with a good uniformity over a large area. e-f, AFM images of the surface topography of Cr patterns with and without SPEL: (e) 13 nm high as-patterned pads (SEM images in a-b), and (f) 35.5 nm high round particles after SPEL (SEM images in c-d)
On the other hand, the center location of the Cr dot did not change after all the processing, indicating the adhesion between the Cr and the HSQ is excellent. This is because HSQ bears a surface energy similar to SiO$_2$ (typically 1-2 J/m$^2$ [103]) after oxygen plasma treatment [104] due to the surface modification with hydroxyl groups [105, 106], and thus wets well the molten Cr. Our patterning technology can achieve good uniformity over a large area, which was about 5.5×5.5 mm$^2$ by stitching adjacent exposed regions [107] and could be extended a much large area by a scanning laser beam.

Atomic force micrographs (AFM) of the surface of Cr dots before and after SPEL on HSQ/PET (Figure 3.6 e-f) show that the height of the metal particles after SPEL was increased from ~13.0 nm to ~35.5 nm while the lateral size was decreased (SEM images of Figure 3.6 a-d), with the total volume of the Cr dots kept constant.

From the results above, it is clear that the improved patterning with a HSQ layer are due to: (a) HSQ’s high melting temperature, which not only guarantees HSQ not to melt during the processes but also prevents the PET substrate from melting, (b) HSQ’s high O$_2$ etching resistance, (c) HSQ’s high surface energy and wetting ability to molten Cr, and (d) HSQ’s excellent surface adhesion to Cr.

To quantify the nano-patterning fidelity with and without a thin HSQ layer, Figure 3.7 showed the diameter distribution of the Cr dots on HSQ coated PET, with a diameter deviation of 1.7 nm, while the diameter deviation of the Cr on bare PET (i.e. without a HSQ layer) is 11.3 nm (over 660 % worse).
Figure 3.7 Diameter histograms of Cr dots on bare PET and HSQ coated PET after NIL and SPEL. (a) 11.3 nm (standard deviation) for Cr dots on bare PET. (b) 1.7 nm deviation for the Cr dots on HSQ/PET. The inserts show the schematics and SEM images of corresponding Cr melting results.
3.2.5 Feature size reduction

SPEL has the ability not only to smoothen features with large edge roughness, but also to reduce the feature size. To demonstrate this on plastic PET, we used a four-time shadow-evaporation technique to artificially increase roughness as well as reduce the dot size, and then used SPEL to perfect the Cr dots (schematic shown in Figure 3.8).

![Figure 3.8 Schematics of nano-dot size reduction on HSQ/PET by shadow evaporation and SPEL: (a) nano-holes in UV imprint resist; (b) smaller nano-holes after Cr shadow-evaporation; (c) Cr liftoff on HSQ/PET with reduced size; (d) rounded Cr dots after SPEL.]

First, the residual NIL resist was etched on HSQ/PET, resulting in resist holes of 102 ± 3 nm by 127 ± 3 nm (Figure 3.9 a). Then Cr was evaporated from four directions (~15 nm each) that are 65° to the substrate surface normal and perpendicular to the hole sidewalls, shrinking the opening size from 102 ± 4 nm to 54 ± 4 nm (Figure 3.9 b). The hole edge roughness appreciably increased, due to the rough surfaces of thick irregular Cr
clusters deposited on the hole openings of the polymer. Then, 12 nm thick Cr was evaporated normal to the HSQ/PET substrate and lifted off, with a size of about 60.0 ± 4 nm by 105 ± 5 nm (Figure 3.9 c). Using a single laser pulse at 277 mJ/cm², the metal dots were melted nearly perfect round to 60 ± 3 nm in diameter (Figure 3.9 d).

Figure 3.9 SEM images of 60 nm sized Cr dots fabricated from >130 nm nano-holes: (a) 127 × 149 nm² nano-holes in UV resist; (b) reduced nano-holes of about 60 × 105 nm² after Cr shadow evaporation; (c) Cr on HSQ/PET after liftoff; (d) 60 nm Cr dots after SPEL.

Comparing the final round Cr dots to the initially patterned holes in resist, it is seen that SPEL can render a more than 78 % reduction of the feature area. The results show that the SPEL technique can simultaneously correct reasonably large feature roughness, reduce the pattern size-variation, and also shrink the feature size on plastic substrates.
3.3 Temperature distribution during SPEL

To understand the temperature distributions of each material during SPEL, we did numerical simulation using a commercial software COMSOL. The coordinate origin was set to the left corner of the HSQ top surface, and the Cr dot and the HSQ were assumed bordering at Z = 0. The structure symmetry reduces the calculation to one unit cell of a size of 235 nm by 235 nm with a Cr partial sphere (35.5 nm high and 44 nm in radius) at the center of the cell (Figure 3.10a).

The Cr dot was assumed a partial sphere, absorbing the same energy as in experiment. The simulation used the same geometry of HSQ and Cr as in experiment, but we assumed a 5 µm thickness for PET, which should not affect the simulation accuracy because PET is a poor thermal conductor [108] and does not propagate heat very deep. The parameters for each material at different temperatures were taken from established literature [92, 109-111], except for the temperature-dependent properties of PET (which were not available) and the properties of HSQ (not available, assumed the same as SiO₂).

| Table 3.1 Physical constants and parameters of Cr/HSQ structure in COMSOL simulation. |
|-----------------------------------------------|----------|----------|
| **Physical constants**                        | Cr       | HSQ      |
| Density (kg/m³)                               | 7.15 × 10³ | 2.19 × 10³ |
| Heat capacity (J/(kg·K))                      | 450      | 746      |
| Thermal conductivity (W/(m·K))                | 93.7     | 1.4      |
| Surface emissivity                            | 0.15     | 0.85     |
| Convective heat transfer coefficient (W/(m²·K)) | 50       | 50       |
Figure 3.10 COMSOL simulation to analyze the temperature distribution within Cr/HSQ/PET structure in SPEL. (a) Simulation model. b-g, Spatial temperature distributions at different time points after annealing starts, with the peak values of Cr \(T_{m, Cr}\) and PET \(T_{m, PET}\) given for reference: (b) 5 ns, (c) 20 ns, (d) 25 ns, (e) 120 ns, (f) 1.4 \(\mu\)s, and (g) 400 \(\mu\)s. (h) Transient temperature variation at different depths along the axis of symmetry \((X = Y = 117.5 \text{ nm})\).
From simulation of the spatial temperature distribution (Figure 3.10 b-g) and transient temperature variation (Figure 3.10 h) inside the Cr/HSQ/PET structure, it shows that the highest temperatures were 2212°C at the Cr top surface (above 1907°C -- the melting point of bulk Cr) and 2137°C at the Cr/HSQ interface, but lasted only ~5 ns and cooled quickly. The highest temperature at the HSQ/PET interface was only 350°C for several hundred nanoseconds. The duration of PET heated above 260°C was less than 1.4 µs (Figure 3.10 f), showing that HSQ acted well as a thermal-barrier layer to suppress the maximum temperature and heating time of PET. For the structure with only Cr/PET (without HSQ), the Cr dot at molten state would not only liquefy the PET but could also vaporize it, causing the Cr dots to move randomly, as observed experimentally.

The transient temperature change can be understood from the different heat-transfer modes in the different stages. During the 20 ns laser exposure and briefly afterwards (within ~200 ns), heat conduction dominates because of the presence of a large temperature gradient in Z direction (on the order of 1-10°C·nm⁻¹), leading to drastic change in temperature (first rises quickly and then drops significantly, Figure 3.10 c). Then after about 200 ns, surface convection overcomes the heat conduction, as the temperature gradient vanishes. Since the system has a thin depth, it eventually reaches a uniform temperature in its interior, and cools down exponentially by surface convection. The cooling time constant is related to the thickness, the material density, heat capacity, and convective constant [110], and can be calculated as about 49 ms for HSQ layer. The simulation shows a close value of ~26 ms for the whole system (Figure 3.10 h).

From both the experimental results (Figure 3.6) and simulation (Figure 3.10), it is clear that 450 nm thick HSQ was sufficient to thermally protect PET. For applications
where better flexibility of the substrate is necessary [82, 84, 112], the HSQ layer could be made thinner and patterned into islands [113].

3.4 Summary

In summary, we have proposed and demonstrated a new approach to patterned 2D metal (Cr) arrays of 60 nm uniform diameter on PET substrate using NIL and SPEL. We have experimentally demonstrated that a layer of HSQ is essential to achieve reliable patterning on PET, because the HSQ layer offers excellent thermal protection, good surface adhesion, and etching resistance. With the HSQ layer, SPEL was capable to greatly reduce pattern roughness (from 11.3 nm to 1.7 nm, improving over 660 %) as well as pattern size (78% using shadow evaporation). Additionally, numerical simulation was used to confirm that the HSQ layer could effectively lower the thermal load on the plastic substrate by greatly reducing the peak temperatures and heating duration.

Our approach of using spin-on-glass [114] (HSQ in our case) to integrate NIL and SPEL for feature patterning on plastic substrate is simple, reliable, and compatible with low-temperature processing requirements, and is expected useful in other laser processing techniques on plastic, such as laser-assisted direct imprint (LADI) [115, 116], via hole filling [117], catalyst metal particle patterning [118, 119], re-crystallization of amorphous silicon films [120, 121], etc. This new technology can be scaled to a much larger area by an alternative roll-roll processing and has potential applications in various fields.
Chapter 4

Nanoimprinting Sub-20 Nanometer Features for Potential Electronic Applications

4.1 Introduction

Reducing the critical dimensions of nano-structures, e.g. to sub 20 nm or smaller, can result in many unique and useful electronic features, such as single electron behavior [49], electron tunneling, graphene bandgap opening [122, 123], etc. In this chapter, fabrication approaches for patterning sub 20 nm trenches and ribbons are presented for potential use in novel tunneling transistors and graphene devices.

4.2 Fabrication of 10 nm-wide asymmetric trenches for Si/SiGe heterojunction tunneling transistors (HETTs)

4.2.1 HETTs for better transistor performance

Conventional metal-oxide-semiconductor field-effect transistors (MOSFETs) have a minimum subthreshold slope of $2.3 \times \frac{K T}{q}$ (60 mV/dec at room temperature) due to the thermionic emission of carriers over a potential barrier, as shown in Figure 4.1 a. To reduce the subthreshold slope beyond the classical thermionic-emission limit, which is
very desirable for low power operation, it requires a new MOSFET structure and different operation principles where the subthreshold current is dominated by other transport mechanisms, such as impact ionization [124-126] or tunneling [127-129]. For a better subthreshold behavior, it is necessary to make asymmetric Si/SiGe Hetero-junction Tunneling Transistors (HETT) [130], as shown in Figure 4.1 b.

![Figure 4.1 Comparison of a conventional Si MOSFET and a Si/SiGe heterojunction tunneling FET. (a) The device structure and the band diagram of an N-type Si MOSFET. (b) The device structure and the band diagram of an N-type Si/SiGe HETT transistor.](image)

4.2.2 Fabrication process of asymmetric trenches

To fabricate such asymmetric HETT transistors, one needs to make a SiGe heterojunction trench in the source region with a Si/SiGe interface next to the gate edge within a few nanometers (Figure 4.1 b). However, such stringent alignment accuracy cannot be met by current photolithography tools, nor can be achieved by conventional symmetrical self-alignment of the source and drain with the gate [131-133].
To overcome this alignment challenge, it is preferable to have a reliable self-aligned method to fabricate an asymmetric trench in the source. Previously, self-aligned asymmetric source/drain doping was achieved in different FET structures by combining a vertical and a tilted implant [134] or using a sidewall-spacer gate [125, 129]; but in these methods, the source/drain substrate materials still remained the same and no asymmetric trenches were created. Significantly different from these approaches, our method, initially from Prof. Stephen Y. Chou, directly creates an asymmetric nanotrench right next to the gate and allows using different source/drain materials.

Figure 4.2 Fabrication of self-aligned asymmetric nano-trenches. (a) Si gate testing structure is patterned. (b) Nano-gap is created and aligned to the gate by a Cr shadow evaporation. (c) Nano-trenches are formed by RIE. (d) Cr is removed. (e) Scheme of dependence of self-aligned nano-gap size $G$ on Si gate height $H$ and shadow evaporation angle $\theta$. 

The key steps in our approach are: (a) using the gate as a shadow mask during an evaporation of Cr from an oblique angle to create a gap uncovered with Cr next to the gate, and (b) etching Si substrate using the evaporated Cr as the etching mask to achieve an asymmetric nano-trench in the Si substrate next to the gate (Figure 4.2). The gap size $G$, i.e. the trench width, is determined by the shadow evaporation angle $\theta$ (relative to the normal of the wafer) and the gate height $H$, by $G = H \cdot \tan \theta$.

To test our approach, we used a 200 nm period grating as the gate structure. Particularly, we first fabricated the grating in Si using nanoimprint lithography (NIL) [39, 88, 89], e-beam evaporation, metal lift-off, and RIE. Then a Cr mask with gaps self-aligned to the grating was formed by a shadow evaporation. This Cr layer defined asymmetric trenches during RIE, and was removed after the etching. For completing a HETT structure, SiGe with desired doping level needs to be grown selectively [135-138] in the trench, which is not a part of this work. The details of the above fabrications are described below.

### 4.2.3 Fabrication of sub-20 nm gratings for NIL molds and Si gate

The first fabrication step is to make a nanoimprint mold with sub-20 nm linewidth for the testing Si gate. We fabricated such molds by shrinking the grating linewidth of an existing mold to sub-20 nm in two steps: (1) use of an O$_2$ trimming of a tri-layer resist structure [139, 140] to narrow the linewidth to 35 nm (previously discussed in Chapter 2); and (2) further reduction of the resist grating linewidth (imprinted by the new mold) using a bi-directional shadow evaporation. The fabricated 35 nm grating mold has a good uniformity over a 4” wafer, with the imprinted resist pattern shown in Figure 4.3.
To narrow the opening of the resist trenches from as-imprinted 35 nm to 20 nm, a bi-directional Cr shadow evaporation [71, 72] was used. About 9 nm-thick Cr was evaporated from the two directions which are at 60° to the sample surface normal and perpendicular to the grating lines, and capped the top part of the resist trenches. The gap size was shrunk from 35 nm down to 20 nm (Figure 4.4 a-b). The narrow opening was then used as a mask for deposition of another layer of 15 nm-thick Cr at the bottom of the trench. A liftoff process was then carried out to pattern Cr lines onto the Si substrate (Figure 4.4 c-d). The Cr lines were 20 nm-wide, the same as the narrowed trench opening. RIE (O₂/CF₄/Ar/SF₆ = 2/30/10/10 sccm, 15 mtorr, 300 W, 30 sec) was used to etch into Si for about 40 nm to obtain the straight Si grating structures, and subsequently
the Cr mask was removed using CR-7 Chromium etchant (Cyantek Corp.), as shown in Figure 4.4 e-f. The linewidth of the final Si grating was calculated to be $20.5 \pm 1.7$ nm using a home-made MATLAB code. Clearly, a good fidelity of the narrow grating lines was preserved throughout the whole fabrication process.

**Figure 4.4** SEM images of different steps in fabricating 20 nm-wide Si testing gates. **a-b,** Cr mask on resist gratings. **c-d,** 20 nm-wide Cr on Si substrate. **e-f,** 20 nm-wide gratings in Si. The left images are cross-sectional view, and the right ones are top-view.
Previous work has already demonstrated that the bi-directional shadow evaporation technique can be used for wafer-scale pattern transfer with small linewidth variations [68], in which case the final linewidth was even highly dependent on the evaporation angle as the resist was in triangular profile [68, 72]. In our case, the trench opening size is much less sensitive to the angle, as the trench sidewall can be controlled fairly vertical. Therefore, the bi-directional shadow evaporation technique is expected applicable to wafer scale, making the whole two-step feature-size tuning technique satisfy large-area and repeatable production requirements. Moreover, the two-step feature-size tuning technique provides a great control flexibility of feature sizes, not only in reduction but also in expansion; and it is not limited to only 1D grating structures, but can also be used to 2D pillar or hole structures [140].

The reason why we had to use the two-step linewidth shrinking approach is because just a bi-directional evaporation itself generally cannot offer uniform linewidth reduction, especially when the reduction is large (e.g. over 50 nm), since a thick metal layer introduces large grains or clusters during deposition and thus results in unacceptable linewidth roughness and variations.

4.2.4 Fabrication of self-aligned asymmetric trenches

Using the 20 nm-wide and 41 nm-high Si grating obtained by NIL and etching, we fabricated a 14 nm-wide gap by shadow evaporation of 10 nm-thick Cr from about \( \theta = 20^\circ \) (Figure 4.5 a-b). An \( \text{O}_2/\text{CF}_4/\text{SF}_6/\text{Ar} \) based RIE was used to etch asymmetric trenches into the Si substrate (Figure 4.5 c-d), and then Cr was removed. The desired asymmetric trenches self-aligned to the Si gate were achieved (Figure 4.5 e-f).
Figure 4.5 SEM images of different steps in fabrication to achieve 13 nm-wide asymmetric trenches aligned to one-side of Si gratings. a-b, 13 nm-wide gap created by shadow evaporation at $\theta = 20^\circ$. c-d, Asymmetric trenches etched into Si by RIE. e-f, 13 nm-wide trenches aligned to gratings after removing Cr. The images are side view ($45^\circ$) on the left and cross-sectional view on the right.

In another test, we fabricated a 35 nm-wide and 57 nm-high Si grating structure as the gate, and obtained 24 nm-wide self-aligned nano-trenches using $\theta = 22^\circ$ and 10 nm thick of Cr shadow evaporation (Figure 4.6 a). Similarly, by lowering the Si grating height $H$
to 40 nm and changing the shadow evaporation angle to $\theta = 18^\circ$, we achieved nano-trenches as narrow as 10 nm (Figure 4.6 b).

![Figure 4.6 SEM images of different asymmetric trench widths achieved by tuning shadow evaporation angle $\theta$ and Si grating height $H$.](image)

The alignment accuracy was estimated by measuring the offset of the asymmetric trenches to the grating edges in Figure 4.5 and Figure 4.6, and found about 2-3 nm, which is far better than the alignment capabilities of current lithography tools [2]. The alignment of the trench to the gate edge is determined by the lateral etching behavior during RIE, and can be further fine-tuned. The excellent and reliable overlay accuracy of this simple self-alignment method is clearly better than that of the approaches based on manual alignment.

### 4.2.5 Accuracy in controlling trench widths

The absolute and relative variations of asymmetric trench widths (gap sizes) $\Delta G$ and $\eta_G = \frac{\Delta G}{G}$ are, to the first order approximation, proportional to the gate height variation $\Delta H$ and the evaporation angle variation $\Delta \theta$ through the following equations:

$$
\Delta G = \Delta H \cdot \tan \theta + H \cdot \Delta \theta \cdot \frac{1}{\cos^2 \theta}
$$

(4.1)
\[ \eta_G = \frac{\Delta G}{G} = \frac{\Delta H}{H} + \frac{\Delta \theta}{\sin \theta \cdot \cos \theta} \quad (4.2) \]

Since the coefficients in the equations are functions of the evaporation angle \( \theta \), \( \Delta G \) and \( \eta_G \) vary at different shadowing angles. To see the angle effects, we can set \( H = 50nm \) and plot \( \Delta G \) and \( \eta_G \) vs. \( \theta \) for different \( \Delta H \) and \( \Delta \theta \) (Figure 4.7). The plots clearly show that \( \Delta G \) is smaller for a narrower angle; but the relative error \( \eta_G \) achieves its minimum at 45° and increases significantly when the angle approaches either 0° (\( G \approx 0 \)) or 90°. As seen from the two cases plotted in Figure 4.7 a-b, i.e. \( \Delta H = 3nm \), \( \Delta \theta = 1° \) and \( \Delta H = 5nm \), \( \Delta \theta = 3° \), \( \eta_G \) can be potentially smaller than 10%, but practically may only be tuned <30% when 16° < \( \theta < 74° \) (or <21% when 36° < \( \theta < 54° \)). \( \Delta G \) and \( \eta_G \) can be controlled small simultaneously, e.g. \( \Delta G < 5nm \) and \( \eta_G < 30% \), by keeping \( \theta \) in a certain range, which is 5°-46° ideally and 16°-22° more practically.

The effects of \( \Delta H \) on \( \Delta G \) and \( \eta_G \) are shown in Figure 4.7 c-d, with \( \Delta \theta = 3° \) and \( H = 50nm \). It is clear that the values of \( \Delta H \) not only influence the angle range for achieving small \( \Delta G \) (e.g. smaller than 5 nm), but also set the lower limits of applicable \( \eta_G \). On the other hand, if we fix \( \Delta H = 5nm \) and \( H = 50nm \) but change \( \Delta \theta \), we have \( \Delta G \) and \( \eta_G \) vs. \( \theta \) in Figure 4.7 e-f. They show that the angle windows for \( \Delta G < 5nm \) or \( \eta_G < 30% \) narrow more significantly as \( \Delta \theta \) increases. This means that the variation of the evaporation angle is a more critical factor to influence the variations of trench widths.
Figure 4.7 Dependence of absolute and relative gap size variations $\Delta G$ and $\eta_G$ on shadow evaporation angle $\theta$ with different variations $\Delta H$ and $\Delta \theta$. a-b, $\Delta G$ vs $\theta$ and $\eta_G$ vs $\theta$ for an ideal case and a practical case. c-d, $\Delta G$ vs $\theta$ and $\eta_G$ vs $\theta$ for different $\Delta H$ (assuming $\Delta \theta = 3^\circ$). e-f, $\Delta G$ vs $\theta$ and $\eta_G$ vs $\theta$ for different $\Delta \theta$ (assuming $\Delta H = 5nm$).
To evaluate the variations experimentally, we measured the grating height $H$ from the SEM images, calculated the expected trench sizes $G^*$ from the average of $H$ and experimental values of $\theta$ using $G^* = H \cdot \tan \theta$, and compared $G^*$ to the measured trench gap sizes $G$, as listed in Table 4.1. It is found that the values of $G^*$ and $G$ are close, within ~3 nm error, showing that the gap sizes could indeed be well controlled by $\theta$ and $H$. Besides, the calculated theoretical gap size variations from experimental parameters (equation 4.1) indicate larger errors are expected, mainly because a large but reasonable variation in shadowing angle is estimated, but relatively small errors seemed to happen during the experiments.

Table 4.1 Evaluation of gap size variations of three asymmetric trench samples.

| Sample | Angle $\theta$ ($^\circ$) | Height $H$ (nm) | Measured gap size $G$ (nm) | Theoretical gap size $G^*$ (nm) | Measured gap error $|G^* - G|$ (nm) | Theoretical gap variation $\Delta G$ (nm) |
|--------|--------------------------|----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| #1     | 20 ± 4                   | 41.2 ± 0.8     | 13.8 ± 1.2                 | 15.0                       | 1.2                         | 3.6                         |
| #2     | 22 ± 4                   | 56.9 ± 1.8     | 24.4 ± 0.8                 | 23.0                       | 1.4                         | 5.4                         |
| #3     | 18 ± 4                   | 40.1 ± 1.8     | 10.6 ± 0.9                 | 13.0                       | 2.4                         | 3.7                         |

Sample #1: Figure 4.5; Sample #2: Figure 4.6 a; Sample #3: Figure 4.6 b.

4.2.6 Selective SiGe growth in nano-trenches

To finish the SiGe HETT transistors, one important step is to selectively grow SiGe into the asymmetric nano-trenches. To demonstrate the feasibility of this process, nano-trenches were patterned by NIL of a grating mold and RIE into a Si wafer capped with thermal oxide (Figure 4.8), using imprint resist and evaporated Cr as the etching mask, followed by cleaning and SiGe growth.
In fabrication, a 200 nm pitch, 35 nm wide grating was imprinted to form trenches in resist (NXR 1025) on a Si wafer with 8 nm SiO$_2$, and a bi-directional Cr shadow-evaporation narrowed the trench width to ~20 nm. The Cr and resist masked etching of SiO$_2$ ($O_2/CHF_3 = 1.5/10$ sccm, 15 mtorr, 100W, 1 min 30 sec) and Si ($O_2/CF_4/Ar/SF_6 = 2/30/10/10$ sccm, 15 mtorr, 100W, 1 min 45 sec), forming 55 nm deep 35 nm wide trenches in Si (Figure 4.9 a-b, undercut due to SF$_6$ etch).

![Figure 4.8 Schematics of selective SiGe growth in SiO$_2$ capped Si nano-trenches.](image)

(a) SiO$_2$ on Si wafer. (b) Imprinted nano-trench resists on SiO$_2$/Si. (c) Cr shadow-evaporated onto resist. (d) Etched nano-trenches in SiO$_2$/Si. (e) Cleaned SiO$_2$/Si nano-trenches. (f) SiGe selectively grown in nano-trenches.

After thorough RCA1 and RCA2 cleaning, the samples were grown with Si$_{0.8}$Ge$_{0.2}$ in a rapid thermal chemical vapor deposition (RTCVD) reactor (by Dr. Keith Chung and Prof. James Sturm). The non-selective growth (6 torr, 625 °C, 6 min, SiCl$_2$H$_2$/GeH$_4 = 26/100$ sccm, $H_2 = 3$ slpm) yielded SiGe growth not only in trenches but also on SiO$_2$ (Figure 4.9 c). In contrast, a selective growth with two cycles, each containing a 3 min
normal growth (the above recipe) and an in-situ 5 min HCl etching (6 torr, 625 ºC, 5 min, HCl = 90 sccm, H₂ = 3slpm), would fill nano-trenches without growing on SiO₂ (Figure 4.9 d). The reason is that SiGe grown on amorphous SiO₂ has a slower nucleation/growth rate and faster etching rate than that epitaxially grown in Si, so that the alternating deposition/etching cycles yield selective growth only in Si nano-trenches.

![Figure 4.9 SEM images of selective SiGe growth in Si nano-trenches. (a) Etched Si nano-trenches with Cr/resist mask. (b) 35 nm wide Si nano-trenches with 8 nm SiO₂ (resist removed). (c) Overgrown SiGe without using selective growth. (d) Filled SiGe in nano-trenches using selective growth. (Growth done by Dr. Keith Chung and Prof. James Sturm.)](image)

4.2.7 Summary of fabricating 10 nm asymmetric trenches for HETTs

In this section, we proposed and demonstrated a simple method to pattern an asymmetric nanotrench in the source regions and self-aligned to the gate for HETT transistors, using shadow evaporation and RIE. Different trench widths as small as 10 nm
(35 nm deep) were fabricated by controlling the gate height $H$ and shadow evaporation angle $\theta$, with a good trench uniformity (variation $\Delta G < 5nm$) demonstrated both experimentally and theoretically. The dimension of the gate was reduced to sub-20 nm, indicating a vast device dimension scaling-down potential. We also demonstrated successful selective growth of SiGe in 35 nm wide nano-trenches, showing the feasibility of HETT transistor fabrication. We believe the self-aligned fabrication method for narrow asymmetric trenches will have various applications not only in HETT transistors but also in other semiconductor ICs, as well as in nano-photonics, nano-biotechnology and nanoelectromechanical systems.

4.3 Printing of sub-20 nm wide graphene nano-ribbon (GNR) arrays for graphene transistors

4.3.1 Graphene and graphene nano-ribbons (GNR)

Graphene [141, 142], a two-dimensional carbon crystal [141-144], has been proven superior in many electronic [123, 141, 145-147], optical [148], and biochemical [149-151] applications, because of its intriguingly high conductivity and mobility [141], atomic layer thickness [149, 150], transparency [145, 152, 153], and flexibility [145, 153]. Although graphene can be obtained through various approaches, such as mechanical exfoliation [141], chemical modification [123, 154], and epitaxial growth [155, 156], it naturally bears a zero bandgap [157], and thus has to be modified to achieve a reasonable bandgap [122, 123], e.g. by nano-patterning into ribbons narrower than 20 nm [122, 123].
Various methods, including nano-lithography [158-160], chemical derivation/assembly [123, 161], and carbon nanotube unzipping [162, 163], have been used to reduce and control the graphene nano-ribbon (GNR) widths, but it still lacks a method to uniformly pattern nano-graphene ribbons over an entire substrate. An alternative approach is to put functional pre-defined graphene patterns only in the active device areas yet over entire wafer (“graphene on demand”). Based on this idea, transfer-printing of graphene has been demonstrated in micro-scale by photolithography [164] and nano-scale by electron beam lithography (EBL) [165], demonstrating good repeatability and uniformity, addressable control, and potential large-scale patterning advantages.

Rather than using EBL, which is serial writing based and thus time-consuming and low-throughput, here we report a method of nano-patterning sub-20 nm wide GNR arrays completely based on nanoimprint lithography (NIL) [88], which includes fabrication of 4” wafer NIL mold of sub-20 nm wide trenches, direct NIL-patterning of GNR on graphite, and transfer-printing of GNR arrays to Si wafers.

4.3.2 Fabrication process of GNR arrays

The fabrication of graphene nano-ribbons consist of three key steps (Figure 4.10): (i) UV imprint using a double-layer resist on fresh-cleaved highly ordered pyrolytic graphite (HOPG) (Figure 4.10 a-b); (ii) pattern nano-graphene ribbons by oxygen plasma reactive ion etching (RIE) and stripping imprint resist (Figure 4.10 c); (iii) contact HOPG with a SiO₂ substrate (Figure 4.10 d) and transfer-print graphene ribbons on SiO₂ with applied external voltage (Figure 4.10 e).

But before the above graphene processing steps, we need to fabricate a NIL mold with 20 nm wide nano-trenches, which was achieved by a two-step feature-size trimming
method [166]. The first trimming, where the linewidth was reduced from 120 nm to 35 nm, created a 4” daughter grating mold (discussed in Chapter 2). And the second trimming step, where the linewidth was reduced from 35 nm to 20 nm, created a 4” grand-daughter trench mold.

![Diagram of patterning and transferring of nano-graphene ribbons](image)

Figure 4.10 Schematics of patterning and transferring of nano-graphene ribbons. (a) HOPG substrate cleaned with scotch tape. (b) Graphene ribbons patterning on HOPG by UV nanoimprint lithography and oxygen RIE. (c) Imprint resist removal to expose graphene ribbons. (d) Graphene ribbons attached to SiO₂/Si wafers. (e) Graphene ribbons transfer to SiO₂/Si.

### 4.3.3 Fabrication of a sub-20 nm trench mold
In the second trimming step (Figure 4.11), a bi-directional shadow evaporation technique was used to shrink the feature, and RIE was used to transfer the narrow feature to the underlying fused silica substrate.

Figure 4.11 Schematics of fabricating a nano-trench mold in fused silica. (a) Nanoimprint on fused silica with daughter grating mold. (b) Bi-directional Cr shadow evaporation to narrow the trench width of resist mask, followed by RIE residual layer. (c) RIE with Cr/resist as mask to etch into fused silica. (d) Resist removal and surface cleaning to achieve a granddaughter trench mold.

First, sub-15 nm thick residual resist (Nanonex NXR-1025) was managed by adjusting spun-on resist thickness (~145 nm) in NIL (150 PSI, 130 °C, 3 min) with the 35 nm wide daughter mold, allowing minimized resist etching and high-fidelity pattern transfer. Then, the Cr shadow evaporation angle (70° from substrate surface normal) and thickness (~10 nm each direction) were tuned to narrow the resist trench to ~18 nm
(Figure 4.12 b). Finally, a pure CHF$_3$ RIE (10 sccm, 300 W, 4.5 mtorr, 10 min, Plasma-therm PD 2486) was used to transfer the pattern to fused silica, creating ~18 nm wide, ~60 nm deep trenches, after a brief oxygen RIE (10 sccm, 50 W, 2 mtorr, 30 sec, Plasmatherm SLR 720) of residual resist. The fabricated 4” fused silica mold (Figure 4.12 d-f) was also treated with mold-release agent (Nanonex NXT-110).

Figure 4.12 SEM images of fabrication steps for an 18 nm wide narrow trench mold. a-c, Cross-sectional images of SiO$_2$ monitor sample: (a) as-imprinted 35 nm wide trenches in resist using fabricated narrow grating mold, (b) bi-directional Cr shadow evaporation defined 18 nm wide gap Cr mask on resist, (c) 18 nm wide, 60 nm deep narrow trenches etched into SiO$_2$. d-f, Final 18 nm wide trench mold fabricated in fused silica.
4.3.4 Nano-patterning graphene ribbons

With the 20 nm linewidth granddaughter mold, we performed the three-step processing for GNR patterning and printing.

In step (i), a HOPG block (SPI-1, 10×10×0.2 mm³, Structure Probe, Inc.) was cleaved with Scotch tape to achieve a clean, fresh, and flat surface. Then UV NIL (100 PSI, 3 min, UV 10 sec) was performed with the fabricated fused silica trench mold (diced to 8×8 mm² to fit onto HOPG) to pattern sub-20 nm wide gratings in a double-layer resist (60 nm top-layer Nanonex NXR-2030, 60 nm sub-layer NXR-3022). Imprint resist was used as the etching mask rather than metal, because the processing was simpler and free from metal contamination (e.g. from metal liftoff). The double-layer UV resist was used rather than thermoplastic resist, because of its better feature fidelity (less feature distortion from heating), high HOPG etching selectivity (top UV resist NXR-2030 is Si-containing and resisting to oxygen etching), and easy resist removal (resist NXR-3022 is water-soluble and free from harsh resist remover), all benefiting reliable pattern-transfer.

In step (ii) to pattern the GNR arrays, an RIE (Plasma-therm PD 2486) step was used to remove the residual top-layer resist (O₂/CHF₃ = 1/10 sccm, 150 W, 5 mtorr, 6 min) and etch through the sub-layer resist and the HOPG (10 sccm O₂, 75 W, 2 mtorr, 8 min). The resist pattern on a silicon control sample processed under the same condition as HOPG is shown in Figure 4.13. Then the double-layer UV imprint resist was removed by 1:1 mixed methanol and deionized water.
Figure 4.13 SEM images of 18 nm wide grating patterns on Si substrate after: a-b, UV nanoimprint lithography with 18 nm wide trench mold, c-d, O$_2$/CHF$_3$ and oxygen RIE to etch residual resist layers.

The GNR features (30 nm high and 18 nm wide) patterned on the HOPG stamp were studied by atomic force microscopy (AFM) image (Figure 4.14 a) and SEM image (Figure 4.14 b), respectively. The GNR patterns on the stamp span uniformly over isolated areas of >5,000 µm$^2$ (~900 µm$^2$ shown in Figure 4.14 c for visualization), sufficient to fabricate functional devices and circuits, e.g. transistors, bio-sensors, nano-optics, etc., for research demonstration purposes.

In this work, the GNR patterning area was limited to 20-30% coverage on the stamp by defects during the NIL step, which were generated by two main factors: (a) non-flat HOPG surface, and (b) non-uniform resist flow during imprint caused by HOPG bending.
due to its low shear modulus (2-4 GPa [167, 168], i.e. >20 times smaller than silicon [92]). By better smoothing the HOPG surface and adjusting the imprint parameters, the defects can be significantly reduced and a good GNR area can be increased. With the fabricated 4” imprint mold, the same technology can be extended to wafer scale, if a wafer scale of HOPG wafers or epitaxial graphene wafers are available.

Figure 4.14 Patterned graphene ribbons on HOPG after resist removal. (a) Side-view of AFM images (2 × 2 μm²). b-c, Top-view SEM images.
4.3.5 Transfer printing of graphene ribbons

In processing step (iii), the electrostatic force assisted printing transferred the GNR from the patterned HOPG stamp to a SiO$_2$ wafer substrate. A home-made setup was used, consisting two Al holders for the wafer and the stamp. The wafer holder and stamp holder mechanically bonded and electrically connected to the wafer (Si resistivity 0.01-0.02 Ω·cm, 5 nm SiO$_2$) and the HOPG stamp, respectively. In exfoliation, the stamp holder was first mechanically pressed onto the wafer, causing an initial contact between the GNR on the stamp and the SiO$_2$ surface of the wafer. Then a 2 V voltage was applied between the stamp and the SiO$_2$ surface for 1 min (with ~20 N holding force). The polarity of the voltage was not observed to affect transfer printing, as it does not influence the magnitude of the electrostatic force. Finally, the wafer was removed and the voltage was turned off.

The mechanical holding pressure is calculated as ~37 psi, using an estimated contact area of ~77 mm$^2$, which includes both the unpatterned graphite (~75 mm$^2$, i.e. 70-80 % of 100 mm$^2$ stamp) and graphene ribbon areas in patterned regions (~2 mm$^2$, i.e. 20-30 % of stamp area times the ribbon duty cycle 0.09). On the other hand, the electrostatic force applied between the graphite and Si substrate can be calculated as ~200 psi using

$$P = \frac{\varepsilon_0 \varepsilon_r V^2}{2 d^2}$$

(5 nm SiO$_2$, voltage 2V), derived from a simplified plate capacitor model. Clearly the electrostatic force is much larger than the pressing force, and allows a uniform pressure in micro/nano-scale in contact areas over the entire sample [169]. Once a good and uniform contact is made, the GNR can be adhered to the clean SiO$_2$ surface of the wafer. With the good adhesion, when the stamp and the wafer are separated, a thin
layer of GNR is attached to the wafer and is exfoliated from the stamp. In comparison, only ~10% as much graphene was transferred without applied voltage probably due to poorer contact, showing the critical role of electrostatic exfoliation in pattern transfer.

After electrostatic exfoliation, 18 ± 2 nm graphene ribbons were transferred to the SiO$_2$/Si wafer (Figure 4.15). Compared to other patterning approaches such as chemical derivation [123] and EBL writing [165] which inherently have a large size variation and/or line-edge roughness, nanoimprint, in combination with other techniques [72, 81, 97], is capable of patterning the nano-ribbons more accurately and uniformly (Figure 4.15 a-b), which are critical for homogeneous GNR device performance.

In this work, the current largest transferred GNR area was about 500 µm$^2$ (~130 µm$^2$ shown in Figure 4.15 b), smaller than that patterned on the stamp. The reason could be attributed to imperfect contact between SiO$_2$/Si wafer and HOPG stamp, caused by defects on the stamp and/or non-parallel alignment of the stamp to the Si wafer.

We observed that the thickness of transfer-printed graphene nano-ribbon arrays was 1-5 nm (from SEM images, Figure 4.15 d) in some areas (spots of ~200 µm$^2$), however in other areas additional graphene layers (20-60 nm thick) were detached from the stamp and transferred onto SiO$_2$ (Figure 4.15 c). These few-layer graphene ribbons (Figure 4.15 d) were 5-10 µm long, sufficient to make functional devices. The undesired additional graphene layers (Figure 4.15 c) could be reduced or eliminated by minimizing HOPG stamp bending in exfoliation and better contacting stamp with SiO$_2$. The GNR production yield and uniformity could be improved by cutting the GNR arrays on the HOPG stamp into designed transistor lengths, which should allow a more uniform local contact and better exfoliation.
4.3.6 Summary of nano-graphene ribbon patterning

In this section, we have proposed and demonstrated a method of patterning 18 nm wide graphene ribbons on HOPG by NIL (over an area of >5,000 $\mu$m$^2$) and transferring them to SiO$_2$/Si substrate via electro-static force assisted bonding. We believe the yield of the patterned GNRs could be further improved by optimizing the transfer-printing setup and parameters. Besides, the tri-layer shrinking and shadow-evaporation techniques in principle can be optimized to reduce the GNR width to sub-10 nm regime for larger graphene bandgap. Our method is also convertible to a roll-to-roll [170] based NIL
process, and can be used to pattern graphene produced by other methods, such as chemical derivation [154], catalyzed growth [156], and so on.

4.4 Summary

In this chapter, we combine NIL with tri-layer resist feature-trimming and bi-directional shadow evaporation techniques to nano-pattern critical features for HETT transistors and GNR transistors, and demonstrate sub 20 nm NIL-patterning of HETT gates and GNR ribbons. Using a single-side shadow evaporation, we also fabricated sub 10 nm self-aligned asymmetric trenches for HETT transistors. The ultra-fine NIL nano-patterning capabilities can be applied to many other fields.
Chapter 5

Si Nanowire Growth on Amorphous Substrates Using Nano-patterned Host-Mediated Catalyst

5.1 Introduction

In the past several decades, the dimensions of electronic devices have been reduced to nanoscale, but traditional optical lithography based top-down fabrication methods are inherently not capable of meeting the requirements of further dimension miniaturization [2]. As alternative approaches, bottom-up methods (sometimes combined with top-down lithography) using synthesized building blocks, such as Si nanowires (Si NWs) [171, 172] and carbon nanotubes (CNTs) [173], are viewed as promising strategies for future large-scale systematic integration [174]. Si NWs are semiconducting and compatible with present semiconductor fabrication technologies, and thus have become a promising candidate for building integrated devices and circuits [172, 175-177]. Besides, Si nanowires (NWs) have many other applications in a broad spectrum of fields [174] such as photonics [178], mechanics [179, 180], and bio/chemical sensing [181, 182], to name a few.
For many applications of Si NWs, the NWs are required to be straight and have well-controlled geometry, orientation, and location. However, a key challenge has been that such properties are missing for NWs grown on amorphous substrates. In this chapter, we present a new approach, termed “growth by nanopatterned host-medicated catalyst” (the NHC growth), to solve the problem.

5.2 Chemical vapor deposition (CVD) based SiNW growth

The conventional methods to grow SiNWs include the Vapor-Liquid-Solid (VLS) method [171], laser ablation [183, 184], evaporation [185], solution synthesis [178], etc. Among them, VLS growth is the most widely used, because it provides the best control of the diameters, lengths, locations, and orientations of the NWs.

5.2.1 Vapor-liquid-solid (VLS) growth

In a typical VLS growth (Figure 5.1), a Si (or other semiconductor materials [186-189], e.g. Ge, InP, GaAs, GaN, ZnO, etc.) substrate is used for the epitaxial growth, and Au (or other metals [190, 191] such as Pt, Ag, Pd, Al, Cu, etc.) is used as the catalyst.

Figure 5.1 Vapor-liquid-solid (VLS) SiNW growth mechanism on Si substrate [171].
The VLS growth is usually based on chemical vapor deposition (CVD). For Au catalyzed Si growth, Au particles are deposited on Si at selective locations as the catalyst, and stabilized at a desired growth temperature, e.g. 400-1100ºC. The growth temperature is selected above the eutectic temperature of the semiconductor-metal binary system, and optimized according to the chemical properties of the precursor gases, the desired growth rates, growth morphologies, and many other parameters. In the VLS growth, there are several critical stages [192]: (1) alloying of Au with Si substrate to form liquid AuSi alloy, which starts at the Au-Si eutectic temperature 363 ºC [193]; (2) mass transport of Si precursors (such as SiCl\textsubscript{4} or SiH\textsubscript{4}) gases; (3) chemical adsorption and decomposition of Si precursor molecules at the vapor-liquid interface; (4) incorporation and diffusion of Si atoms in the liquid AuSi phase; (5) supersaturation of AuSi alloy and resultant crystallization of Si atoms into solid phase templated on the substrate lattice.

As a result, Si nanowires grow epitaxially, and vertically if a Si (111) substrate is used, at the locations where Au nano-particles are deposited, with their diameters controlled by the Au particles.

### 5.2.2 SiNW growth CVD setup

![Figure 5.2 Schematic of a CVD setup for SiNW growth.](image)
An atmospheric CVD setup was home-built and used to grow SiNWs (schematics and optical pictures shown in Figure 5.2 and Figure 5.3). A quartz tube furnace (Lindberg/Blue M three-zone furnace) was used, with three inlets connecting to pure H\textsubscript{2} (99.9995 %, Messer MG Industries), carrier Ar (99.9999 %, Matheson Tri-Gas, Inc.), and inert gases (house N\textsubscript{2} and Ar). During the growth, the quartz tube furnace was sealed airtight, heated up to 1000 °C for ~40 min with flowing pure Ar, and then stabilized for 10 min, before SiCl\textsubscript{4} vapor and H\textsubscript{2} were introduced into the reaction tube. The SiCl\textsubscript{4} vapor, carried by 0.5 slpm Ar from liquid SiCl\textsubscript{4} source (99.998 %, Sigma-Aldrich Co., held in a glass flask in a fume hood), and H\textsubscript{2}, flowed nominally at 0.5 slpm, were mixed into the quartz tube as the precursors. Another 1 slpm pure Ar gas line was used as diluent. The residual reactant gases were neutralized by flowing through a flask with NaOH solution (in the fume hood). The SiCl\textsubscript{4}/H\textsubscript{2} ratio was calibrated about 8.5 %.

![Figure 5.3 A home-built SiNW growth setup: (a) over-all view; (b) SiCl\textsubscript{4} source and NaOH reactor in fume hood; (c) control panel with valves and flow-meters; (d) tube furnace.](image-url)
After the growth, the gas lines of H₂ and carrier Ar (with SiCl₄ vapor) were shut off immediately, and the setup was stabilized for 5 min with pure Ar flowing at nominally 0.5 slpm. Then the furnace was ramped down to room temperature, and the samples were retrieved.

5.3 Conventional SiNW growth on amorphous substrates

Although epitaxial growth on Si (111) can achieve vertically aligned Si NWs of uniform length, diameter and wire-orientation, as well as single wire per catalyst dot (one-to-one growth) [194-196], the substrate is conducting and thus all synthesized NWs are electrically connected. Therefore, it is often necessary to select, cut, and manipulate individual nanowires and make complex contact patterning (e.g. by e-beam writing) to fabricate a functional SiNW device. The procedure is typically low-yield and time-consuming, and thus not suitable for real high-throughput integration.

For many applications, the NWs are required to be grown on amorphous and insulating substrates with straightness and well-controlled geometry, orientation, and location so that they can be directly used for device integration. Despite enormous efforts, however, a central challenge has been that the NWs grown on amorphous substrates do not have such properties.

5.3.1 Non-uniform nanowires grown on amorphous substrate

The growth on an amorphous substrate with the conventional Au nanodot catalyst, unfortunately, results in uncontrollable NW growth, including the following aspects: (1) curved and twisted shapes, (2) large variations in NW’s length, diameter, and wire-
orientation (could be orders of magnitude worse than epitaxial growth), and (3) several wires per catalyst dot [197-199].

As an example, a typical growth (1000°C, 5 min, SiCl₄/H₂) using a 1.3 nm thick unpatterned Au film on SiO₂ resulted in an entangled network of NWs (Figure 5.4), clearly not satisfying the addressable control requirement of SiNW devices.

![SEM image of SiNWs grown using 1.3 nm thick Au film.](image)

Using NIL-patterned Au nano-dots (200 nm pitch, 4.3 nm-thick, 62×51 nm² in size, Figure 5.5 a), clearly more regular NWs were grown (1000°C, 5 min, SiCl₄/H₂, Figure 5.5 b-c). However, the Si NWs had curvy shapes and a broad distribution of lengths (253 % deviation), diameters (21 % deviation), and orientations (section 5.4), with an average 2.5 Si NWs per patterned Au dot.
Figure 5.5 SEM images of SiNWs grown using single-layer Au: (a) as-patterned 4.3 nm thick Au particles; b-c, top-view and side-view images of grown nanowires.

5.3.2 Challenges of growing uniform nanowires on amorphous substrate

In our view, the causes of the non-uniformity on amorphous substrates are related to the behavior of the Au catalyst and its interplay with the underlying substrate during a conventional VLS growth. The issues of much more uncontrolled growth on amorphous substrate are from the following three aspects (Figure 5.6).
First, a pure metal (e.g. Au) catalyst dot does not wet on an amorphous substrate [200], and thus often breaks into multiple smaller catalyst dots before and during growth (Figure 5.6 a-b), driven by surface energy minimization [198, 199, 201, 202]. Clearly seen in Figure 5.5 a, the as-patterned thin Au particles on SiO₂ are non-continuous [203, 204], hence providing multiple seeding particles at each patterned site instead of one. This leads to growth of multiple NWs per site with their diameter determined not by the original Au dot but by the broken-up dots, which are random in size and location [198, 199]. The growth on Si substrate is much easier, because Au reacts with Si to form wetting AuSi alloy [205] and thus adheres much better.

Second, the NW length depends on the incubation time [198, 199] and nanowire growth rate [192, 206]. On amorphous substrates, the incubation time depends on the time for the NWs to become saturated with the Si atoms from the precursors (Figure 5.6 c-d), which varies drastically due to random particle size and leads to the NW length difference. On a Si substrate, the AuSi alloy particles are saturated with Si prior to growth, minimizing the difference in incubation time.

Third, neither the Au catalyst dot nor the underlying amorphous substrate provides a preferred crystal orientation, hence there is no preferred direction for Si growth (Figure 5.6 e-f), resulting in a random growth orientation. In contrast, the Si substrate provides the template for Si epitaxial growth and controls the orientation much better.
5.4 Growth using nanopatterned host-mediated catalyst (NHC)

In this section, a new approach to solve the problem of non-uniform growth on SiO₂ is proposed and experimentally demonstrated. The approach, termed “growth by nanopatterned host-mediated catalyst” (NHC Growth), does not use a pure metal catalyst on an amorphous substrate in a vapor-liquid-solid growth, but rather a mixture of a metal catalyst and the material (Si in our case) to be grown. The to-be-grown material serves as
a host to the metal catalyst to (a) ensure one single metal catalyst dot per growth site, (b) prevent the catalyst dot break-up during the growth, (c) provide an additional material source for the NW growth, and (d) crystallize the metal catalyst to control NW orientation.

5.4.1 NHC growth of SiNWs

![Figure 5.7 Schematics of fabricating nanopatterned host-mediated catalyst (NHC) for controlled growth of SiNWs: (a) NHC catalysts arrays are NIL-patterned on SiO$_2$/Si, with Au/$\alpha$-Si/Au/$\alpha$-Si thin layers deposited from top to bottom. (b) Au and Si react to form alloy droplets and eventually coalescence into one single alloy ball during annealing. (c) Au and Si precipitate from the AuSi alloy during cooling and solidify into one single Au particle covered by a Si shell. (d) Au particles are exposed after wet-etching of Si shell; (e) SiNWs grow from Au particles.](image)

Specifically, the NHC process has four key steps (Figure 5.7): (a) patterning multi-layer nanosquares of the host material (e.g. Si) and the catalyst (e.g. Au) on an amorphous substrate, (b) pre-growth melting of the multilayer, (c) cooling and solidification, turning each nanosquare into a single Au dot surrounded by a Si shell and

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crystallizing the Au dot with the (111) orientation normal to the substrate surface, and (d) etching away the top part of the Si shell to expose Au dot for growth.

The formation of a single Au dot is due to full coalescence of AuSi alloy in mediated meting and subsequent complete separation in cooling. During VLS growth of NWs, the Si base provides an additional Si source for growth and helps Au to be saturated with Si. As shown later, this method makes the grown NWs have uniform diameter and length, straightness, and preferred wire-orientation and location.

In one of our NHC experiments, the multilayer nanosquare catalyst on a SiO$_2$ substrate is a patterned array of Au/α-Si/Au/α-Si (nominally 2.9/3.8/3.4/5.7 nm thick, 126 × 124 nm$^2$ in size) (Figure 5.8a). They were fabricated by formation of nano-holes in a resist by nanoimprint lithography (NIL) [41, 88], e-beam evaporation of Au/Si multilayers onto the imprinted resist, and lift-off. The pre-growth melting was at 1100 °C for one hour (ramping-up rate ~20°C/min, cooling-down rate 5-7 °C/min, N$_2$ ambient, atmospheric pressure). The sample was cooled naturally in air (Figure 5.8 b). A mixture of HF and nitric acid (HF: HNO$_3$: DI H$_2$O = 1:2:20) was used to remove the top Si shell (and unintentionally grown SiO$_x$), exposing the Au nano-particles for growth (Figure 5.8 c). SEM inspections of the samples show that after the annealing one single Au dot was formed at the center of each patterned square (sample A, Figure 5.8 b-c).
Figure 5.8 Top-view SEM images of NHC catalysts at different fabrication steps: (a) as-patterned on SiO₂; (b) after annealing (cross-sectional SEM shown as inset); (c) after wet-etching of Si shell.

Using the NHC samples, Si NWs were grown at 1000 °C for 5 min (SiCl₄/H₂ ratio 8.5 %, Ar as carrier and diluting gases). As a result of one-to-one patterning (one per each site) of Au particles, one Si NW was grown from each site (Figure 5.9). The formed Au nano-dots had an average diameter of 75 nm and a height of 38 nm, and the grown Si
NWs have an average diameter of 81 nm and length of 248 nm. The side-view SEM image (Figure 5.9) shows that the Si NWs were straight, vertically aligned, and uniform in length and diameter.

Figure 5.9 SEM images of SiNWs grown using NHC catalysts: (a) side-view; (b) top-view.
5.4.2 Necessity of annealing and etching in NHC method

In comparison, as-patterned and annealed multi-layer samples (with Si-cap shell) were used for Si NW growth (Figure 5.10 and Figure 5.11).

For the as-patterned multi-layers (Figure 5.10), messy, curvy, and highly non-uniform nanowires were grown from the patterned sites. This is probably because the temperature-stabilization stage (~40 min temperature ramp-up to 1000 °C and 10 min stabilization) in effect annealed the multi-layers, creating Au particles with the largest at the center. As a result, the thickest NW grew at the pad center (illustrated in Figure 5.10 a-c). However, the duration of the annealing was not sufficient to fully merge the alloy droplets, leaving uncoalesced smaller ones to grow thinner and curvy nanowires surrounding the big ones.

Figure 5.10 Schematics and results of SiNW growth using as-patterned multi-layer catalysts.

a-c, Schematics showing the agglomeration of multi-layer structures under heating prior to growth leads to curvy nanowires. d-e, Top-view SEM pictures of multi-layer catalysts (Au/α-Si/Au/α-Si = 1.9/3.7/2.4/5.0 nm) and grown SiNWs, respectively.
For the annealed sample without etching Si cap (Figure 5.11), single Au particle was formed and correspondingly only one nanowire was grown from each site, but some sites were missing nanowires (Figure 5.11 d-e). The reason could be attributed to the partial blockage of precursors by the Si shells enclosing the Au particles. The occasional Si NW growth is possibly because the Si (or SiOₓ) shells can be etched by the SiCl₄ (or HCl, resultant from reaction of SiCl₄ with H₂).

Comparing the SiNWs grown from the as-patterned (Figure 5.10) and annealed samples (Figure 5.11) to the NHC samples (Figure 5.9), it can be concluded that both annealing and wet-etching of Si capping layer were necessary for reliable one-to-one growth of SiNWs.
5.4.3 Diameter and length distributions of NHC-grown Si NWs

To study the uniformity of NHC growth (Figure 5.9), the lengths and diameters of 44 nanowires across 5 regions were measured using cross-sectional SEM images (Figure 5.12). The measured diameter of NHC nanowires was $80 \pm 3$ nm (3.7% deviation, Figure 5.13a) and the length was $248 \text{ nm} \pm 11$ nm (4.4% deviation, Figure 5.13b). The good NW uniformity (diameter and length deviations $<5\%$) span the whole sample (2.5 mm size), showing the potential application of the NHC method for a wafer-scale growth.
5.4.4 SiNW diameter control using NHC growth

Another advantage of NHC growth is that it provides flexibility in controlling the NW diameter. To demonstrate, two different Si/Au samples were used to control the Au
dot diameter: sample B (124 × 101 nm² in area, 2.9/3.8/3.4/5.7 nm of Au/α-Si/Au/α-Si thickness, Figure 5.15 a-b) and sample C (48 × 57 nm², 2.0/3.7/2.4/4.9 nm thick, Figure 5.15 c-d), and the grown Si NWs had diameters of 72 nm and 40 nm, respectively.

Figure 5.15 SEM images of SiNWs grown using catalysts of different sizes. a-b, Sample B: (a) 124×101 nm² NHC catalyst, and (b) corresponding 72 nm nanowires. c-d, Sample C: (c) 48×57 nm² NHC catalyst, and (d) corresponding 39 nm nanowires.

The measured Si-NW diameter, $d_{Si}$, is found to be equal to the Au catalyst diameter

$$d_{Au} = \sqrt[3]{\frac{12}{\pi} \cdot V_{Au}}$$

, calculated using deposited Au volume $V_{Au}$ and assuming a hemispherical shape, within a 2 nm error (Figure 5.16). By controlling the NIL pillar size and Au thickness, we have tuned the Si NW diameter from ~40 nm to ~80 nm. We believe the tuning range can be wider than what we have achieved, possibly down to sub-10 nm regime.
Figure 5.16 The correlation of measured SiNW diameters $d_{Si}$ with diameters of Au hemispheres $d_{Au}$.

5.4.5 Advantages of NIL patterning

In our approach, NIL was used not only for its patterning accuracy, but also for its high-throughput, large-area, and high-density patterning abilities. The spatial density of our NWs is 25 wires/$\mu$m$^2$ for 200 nm period NIL molds, which is much higher than using Au colloids (0.1-1.8 wires/$\mu$m$^2$) [195] or photolithography-patterned Au micro-particles (0.02 wires/$\mu$m$^2$) [207]. The NW density can be further increased by reducing the patterning period.
5.5 Comparison of NHC growth to conventional growth

5.5.1 Comparisons in diameters and lengths

For the NHC growth, the diameter and length were both uniform (only 3.7 % and 4.4 % error), whereas for the conventional growth the diameter was $39 \pm 8$ nm (21 % deviation) and the length was $409 \pm 1036$ nm (253 % deviation), about two orders of magnitude worse (Figure 5.17). The NHC uniformity is also much better than non-patterned Au films [208-210] (>85 % deviation) or colloidal Au particles (typically 10 % ~20 % deviation [197, 211]). Besides, the NHC growth provided addressable one-to-one control of NWs, but the conventional growth yielded average 2.5 NWs each site.
5.5.2 Comparisons in orientations

The NW alignment uniformity is another critical issue for device integration [212, 213]. To characterize the alignment, we measured, using SEM images, the distribution of zenith angles \( \theta \) (the angle of SiNWs tilted from the SiO\(_2\) surface normal, Figure 5.18c), by calculating \( \sin \theta = L_1 / L_0 \) (\( L_1 \), the measured in-plane projection length of a nanowire; \( L_0 \), the average wire length, 248 nm).

![Figure 5.18 Statistics of SiNW angles tilted from the substrate surface normal (angle \( \theta \)).](image)

(a) A model for angle calculation; (b) Angle distribution of conventional approach; (c-d), Angle distribution of NHC approach.
The above calculation works well when $\theta$ is smaller than $70^\circ$, with the theoretical error $\Delta \theta = \frac{\Delta L_1}{L_0 \cdot \cos \theta}$ smaller than $3^\circ$ (assuming $\Delta L_1 = 5nm$). Using the above equation, we found 54% of conventionally grown nanowires (173 NWs in total) were too curvy and not suitable for analysis, while the 46% analyzed NWs had a rather broad orientation distribution, spanning from 0 to $90^\circ$ without a preferred angle (Figure 5.18b). In contrast, most NHC-grown NWs were aligned vertically to SiO$_2$ substrate within a small angle, i.e. 39% of the 496 measured NWs within $10^\circ$, 93% within $50^\circ$, and 99% within $70^\circ$ (Figure 5.18 c-d).

5.6 Mechanism of NHC growth

5.6.1 Pre-growth annealing and crystallization of Au particles

The reason, why the NHC growth on an amorphous substrate has straight silicon NW array with uniform length and diameter, preferred orientation and predetermined location, is that the host material in the NHC growth (a) ensures one single metal catalyst dot per growth site, (b) prevents the catalyst dot break-up during the growth, (c) provides an additional material source for the NW growth, and (d) crystallizes the metal catalyst to control Si NW orientation.

The NHC process for full coalescence of catalyst particles is intrinsically determined by the AuSi alloying process, which is much more favorable than pure Au dewetting. This is because AuSi alloy has a larger volume through incorporation of Si (~3 times at 1100 ºC with a 65 % Si atomic solubility [193]), ~30 % smaller surface energy [214], and a better wetting ability on SiO$_2$ [215] (Figure 5.19 a-b).
Figure 5.19 Mechanisms of controlled catalysts patterning in NHC growth. a-b, Au-Si binary phase diagram with the inserts showing the evolution of NHC catalysts, with the red and blue lines indicating the Si concentration change in AuSi system: (a) during mediated melting, (b) during cooling. (c) A STEM cross-sectional image of annealed NHC particle (after wet-etching). (d) XRD spectra of as-patterned multi-layer and annealed (with Si cap etched) samples showing amorphous and (111) crystalline Au phases, respectively.

During mediated melting (Figure 5.19 a, red arrows), the as-patterned multi-layer nano-islands start to melt at the Au-Si eutectic point (~363 °C) to form small AuSi alloy droplets, which flow and finally merge completely into a single molten AuSi alloy ball with a hemisphere shape.
Upon cooling (blue arrows, Figure 5.19 b), the Si and Au separate from each other completely, due to their negligibly small mutual solid solubilities (<2×10⁻⁴ % Au in Si [216] and ~0.1 % Si in Au [217]), with Si forming a shell surrounding Au due to Si’s smaller surface energy than Au [214]. This fact is clearly seen in our transmission electron microscopy (TEM) image (Figure 5.19 c), showing one single Au ball forms on a Si base (after Si top shell etched).

The x-ray diffraction (XRD) spectra (Figure 5.19 d) show that the Au dot in NHC is crystallized with (111) direction normal to substrate surface during pre-growth annealing. It has been known that annealing of a face-centered cubic (FCC) metal (such as Au) or diamond-lattice material (such as Si) leads to the preferred crystallization of (111) plane parallel to substrates [200, 218-220], because (111) planes are most densely packed and thus the surface/interface energies are minimized [200]. After co-annealing with Au, the thin Si base layer is expected to be (111) crystallized, which has been demonstrated in both micro-scale [221, 222] and nano-scale [223]. In our case, the (111) Si texture is not clear from XRD, probably because the layer is too thin (<13 nm) and embedded with some <5 nm Au particles precipitated from annealing (Figure 5.19 c). During Si NW growth, Au reacts again with the Si layer to form a single catalytic alloy ball, and the excessive Si or Au is expected to remain as a (111) textured seeding layer, which guides the growth of Si NWs into <111> orientation and vertical to the substrate.

Moreover, the Si shell could provide the Si source during the early stage of NW growth for AuSi alloy saturation and thus eliminate the difference in NW incubation time [198, 199], further unifying the NW growth.
5.6.2 Surface energy minimization

![Image showing multi-layer catalyst structure](image)

Figure 5.20 Schematics of Multi-layer catalyst structure for surface energy comparison: (a) multi-layer catalysts before annealing; (b) AuSi alloy ball after annealing. $S_{A1}$ and $S_{A2}$, Au-air interface area; $S_{S1}$, Si-air interface; $S_{A3}$, AuSi-air interface; $S_{A4}$, AuSi-Si interface (sidewall area); $S_{A5}$, AuSi-SiO$_2$ interface (bottom surface); $S_{S2}$ and $S_{S3}$, Si-air interface after annealing.

In NHC catalyst patterning, the minimization of surface/interface energies naturally reshapes the multi-layer catalyst into hemispheres during annealing. To see how stable the Au-Si systems are before and after annealing, the system energies are both calculated at 1100 °C (Figure 5.20), with a total energy $\gamma_1$ for the non-annealed multilayer structure and $\gamma_2$ for the annealed AuSi alloy ball and Si base.

\[
\gamma_1 = \sigma_{Au} \cdot (4S_{A1} + S_{A2}) + \sigma_{Si} \cdot (S_{A4} + S_{S1})
\]

\[
\gamma_2 = \sigma_{AuSi} \cdot (S_{A3} + S_{A4} + S_{A5}) + \sigma_{Si} \cdot (2S_{S2} + S_{S3})
\]

where $\sigma_{Au}$, $\sigma_{Si}$, and $\sigma_{AuSi}$ are the Au, Si, and AuSi surface tensions (for simplicity, assuming $\sigma_{Au}$ for Au-Si, Au-air, and Au-SiO$_2$ interfaces, $\sigma_{Si}$ for Si-air and Si-SiO$_2$ interfaces, and $\sigma_{AuSi}$ for AuSi-air and AuSi-SiO$_2$ interfaces), respectively.

Using the experimental geometrical parameters (Figure 5.8) and published surface tension data [214], namely $\sigma_{Au}$ 1.11 J/m$^2$, $\sigma_{Si}$ 0.746 J/m$^2$ (at Si melting point 1414 °C),
and $\sigma_{AuSi} = 0.77 \text{ J/m}^2$ (~65 % Si in AuSi alloy at 1100 °C), $\gamma_1$ and $\gamma_2$ are calculated as $7.5 \times 10^{-14} \text{ J}$ and $3.4 \times 10^{-14} \text{ J}$, respectively. Obviously, $\gamma_2$ is much smaller than $\gamma_1$, meaning the alloy ball structure is more thermodynamically stable and more favorable than the multi-layers during annealing.

5.6.3 Comparisons of NHC to conventional Au annealing

Previously one-to-one growth of single nanowires has been attempted by annealing patterned Au dots prior to epitaxial growth on Si [224] (and InP [225]), but not on amorphous substrates. Even for epitaxial synthesis, this annealing process was only partially successful, because missing-wire and multi-wire sites were still not eliminated [224, 225]. Besides, the successful annealing only worked under very carefully controlled conditions [224], requiring a large ratio of Au thickness to pad size (0.33 [225] - 0.5 [224]), stringently defined pattern size, and narrowly adjusted pre-growth annealing temperatures (<15 °C error [224]).

If using amorphous SiO$_2$ substrates, however, such a conventional annealing process is expected more difficult, because Au dewets on SiO$_2$ and agglomerates randomly [200] while it reacts with Si substrate to form a wetting alloy and thus adheres much better [205]. The annealing process is also very sensitive to the catalyst shape, the material (catalyst and the substrate), and the temperature, and thus not possible for the simultaneous growth of nanowires with different diameters or on different substrates.

In the NHC process, the alloy ball is fixed by the amorphous Si layer in the pad center without diffusing randomly, naturally guaranteeing a perfect location control with a much larger tolerance on geometry variations (from 50 nm to 120 nm, Figure 5.16). Even with very thin Au (~6 nm) and small thickness-to-pad ratio (0.05-0.08), all the NHC samples
were able to yield uniform Au particles and Si NWs, different from conventional single layer Au sample with a similar ratio (~0.08) but only to obtain random wires. The NHC alloying occurs within the multi-layers but not on the substrate surface, and thus applicable to various substrate materials. Besides, in principle any temperature higher than the eutectic temperature should work in NHC annealing (e.g. $<400 \, ^\circ\text{C}$ demonstrated for co-annealing of Si and Au [222]). A higher temperature is more favorable for a better coalescence, because AuSi alloy has a larger size and a lower surface energy due to its higher silicon concentration [193].

### 5.7 Summary

In this chapter, we have proposed and demonstrated a new approach, NHC growth, to addressably control the growth of Si NWs on amorphous substrates ($\text{SiO}_2$). The NHC NWs are exactly one-wire-per-site, 10-100 times more uniform in diameter and length (<5 % deviation) and far better vertically aligned (70 % within 30°) than conventional grown NWs. Using the NHC growth, we demonstrated Si NWs of a minimum 40 nm diameter and a high density (e.g. $>25$ wires/$\mu\text{m}^2$). Such a controllable growth on amorphous SiO$_2$ is very desirable, and has been demonstrated by us for the first time.

We expect that the NHC growth can be extended to other semiconductor nanowires (Ge, SiGe, ZnO, III-V materials, II-IV materials, etc.), and is applicable on substrates of arbitrary material or crystalline structure, potentially satisfying broad academic and industrial interests. Besides nanowire growth, our approach can also be used to produce controllable crystalline Au particles for other intriguing applications in biochemistry [226], optics [227], electronics [228], and others.
Chapter 6

Nano-patterning for Improving Light Extraction of Light Emitting Diodes (LEDs)

6.1 Introduction

Light-emitting diodes (LEDs) [229-232] are of great interest for their applications in next-generation solid state lighting (SSL) [233-236], including indoor illumination lamps, automobile headlights, traffic lights, laptop and cell phone monitors, etc. Based on the continuous advancement in compound semiconductor crystal growth and related techniques [237-240], III-nitride semiconductors (such as AlN, GaN, InN and their alloys) [230, 241, 242] have emerged as attractive materials for LEDs, due to their easily tunable light emission wavelength ranging from deep UV to infrared [232, 243], chemical stability (and thus long lifetime) [241, 242], and others.

However, one big challenge limiting the use of III-nitride in high-power and high-efficiency LEDs is the low light-extraction efficiency (LEE), which is caused by small light escape cones at the GaN/air interface due to the large mismatch of GaN-air refractive indices. The most popular methods to increase LEE is to enhance light scattering and/or redirect the guided mode into the radiative mode [244-248] by patterning the GaN layer [247-249] or the underlying sapphire (Al₂O₃) substrates [250,
Conventionally, the patterning has been limited to micro-scale and realized by dry etching, and is thus low-efficient, slow, and expensive. In this chapter, we present one effective, inexpensive, and high-throughput method of nano-patterning sapphire substrate using nanoimprint lithography (NIL) and wet-etching.

6.2 Nano-patterning sapphire substrate

To pattern sapphire substrate (PSS), one can either use inductively coupled plasma (ICP) dry etching [252, 253] or chemical wet etching [250, 251, 254]. ICP etching of sapphire can achieve good control of trench/mesa sidewall angle (by controlling power, etching chemistry, etc.) and etching depth, but it is much slower (typically tens of minutes per wafer), more expensive, and equipment intensive compared to wet etching. Furthermore, fast ICP sapphire etching uses high-energy reactive gases (e.g. Cl₂, BCl₃ and Ar based), which easily degrade commonly used polymer and dielectric masks. Therefore, ICP etching typically requires a metal mask, which is not desirable for subsequent contamination-free GaN growth.

Wet etching of sapphire [250, 251, 254, 255] is based on chemical reactions of sapphire with mixed sulfuric acid and phosphoric acid (typically mixed at 3:1) at an elevated temperature (200-400 °C), resulting in a high etching rate (1-10 μm/hour) and an anisotropic profile with preferable etching of c-plane, i.e. (0001) plane [250, 256].

In our approach, NIL and wet etching were combined to achieve nano-patterned sapphire substrates (NPSS) (Figure 6.1). First, 100 nm SiO₂ was deposited by plasma enhanced chemical vapor deposition (PECVD) (Plasma-Therm 790, 2 % SiH₄ in N₂ at 35 sccm, N₂O at 160 sccm, 400 mtorr, 25 W, 250 °C, 5 min) on RCA1 cleaned 2” c-plane sapphire wafers (Figure 6.1 b), and then patterned into 200 nm pitch pillars (~80 nm size)
and 1 μm pitch bars (~250 nm wide, ~750 nm long) by thermal NIL, oxygen RIE residual layer, Cr liftoff (Figure 6.1 d), and CF₄/H₂ RIE. Then Cr was removed by CR-7, and the substrate was RCA1 cleaned (Figure 6.1 e).

![Figure 6.1 Schematics of nano-patterning sapphire by anisotropic wet etching: (a) blank cleaned sapphire wafer; (b) PECVD deposition of SiO₂; (c) NIL on sapphire; (d) Cr nano-dots liftoff; (e) SiO₂ pillar RIE and Cr etch; (f) sapphire wet etching; (g) SiO₂ pillar etch by HF; (h) GaN growth.](image)

The sapphire substrates were etched by 3:1 mixed H₂SO₄ and H₃PO₄ solution (stabilized at ~240 °C), and then the SiO₂ mask was completely removed by buffered oxide etch (BOE 1:6) for 1 min. By controlling sapphire wet etching time (50 sec and 5 min for 200 nm and 1 μm pitch) and thus depth (55 nm and 270 nm), NPSS with flat c-plane bottom surfaces were achieved (Figure 6.2 and Figure 6.3).
Figure 6.2 SEM images of 200 nm pitch NPSS: (a) SiO$_2$ mask; (b) NPSS with SiO$_2$ mask; c-d, Top view and cross-sectional view of NPSS with SiO$_2$ removed.

Figure 6.3 SEM images of 1 μm pitch NPSS: (a) SiO$_2$ mask; (b) NPSS with SiO$_2$; c-d, Top view and cross-sectional view of NPSS without SiO$_2$. 
6.3 GaN growth on nano-patterned sapphire substrates (NPSS)

The NPSS were cleaned by RCA1 and RCA2 (HCl:H₂O₂:DI water = 1:1:5, 80°C), and grown with a GaN LED structure by metal-organic chemical vapor deposition (MOCVD, IQE RF, LLC). From the bottom to the top, the stack consists of a 2 μm thick GaN buffer layer, 2 μm thick n-GaN, six periods of InGaN quantum wells (in total 76 nm thick), 27 nm AlGaN cladding layer, and 800 nm p-GaN layer (with 150 nm heavily doped for contact). Uniform and flat GaN films of ~5 μm thick were grown without appreciable defects on NPSS with flat c-plane bottom surfaces (Figure 6.4). The GaN films on 200 nm- (Figure 6.4 a-b) and 1 μm-pitch substrates (Figure 6.4 c-d) had a small mean roughness of 3.1 nm and 4.3 nm, very close to that of blank sapphire wafer (1.9 nm) (Figure 6.5).

![GaN growth on nano-patterned sapphire substrates](image)

*Figure 6.4 Cross-sectional SEM images showing grown GaN: a-b, on 200 nm pitch NPSS; c-d, on 1 μm pitch NPSS.*
However, in comparison, if the NPSS substrates are patterned to have sharp V-shaped bottom surfaces by over-etching the sapphire c-planes, very poor growth of GaN would result. For example, for a 2” 200 nm pitch over-etched NPSS (4 min sapphire etching) (Figure 6.6 a-b), the GaN did not coalescence, resulting in a very thin (~150 nm) and rough GaN layer (Figure 6.6 c) in some regions and large GaN islands of various sizes and heights (as large as >21 μm) in others (Figure 6.6 d). On the other hand, the GaN growth on 1 μm pitch NPSS (15 min wet etching) (Figure 6.7 a-b) coalesced better, but left many pin-holes at the growth interface and created rough GaN film surfaces (roughness ~14 nm in the best region, but >100 nm in worse regions) (Figure 6.7 c-d).
Figure 6.6 SEM images of 200 nm pitch NPSS with an etched sharp bottom surfaces and corresponding GaN growth. a-b, Cross-sectional view and top view of patterned sapphire. c-d, Grown GaN on sapphire.

Figure 6.7 SEM images of 1 μm pitch NPSS with sharp bottom surfaces and corresponding GaN growth. a-b, Cross-section view and top view of etched sapphire before growth; c-d, Cross-section view and top view of GaN grown on sapphire.
6.4 Fabrication of GaN blue LED devices

To make a GaN LED with the best performance, some fabrication factors have to be carefully controlled, including the GaN etching optimization (mask material and recipe), ohmic contact formation, current spreading, device packaging, etc. In this section, discussions are focused on GaN etching and ohmic contact.

6.4.1 LED fabrication process

Figure 6.8 Schematics of fabricating a GaN LED (sapphire substrate not shown). (a) Grown GaN structure with P-layer on top of N-layer; (b) PECVD SiO₂ mesa patterned by photolithography and RIE; (c) ICP etched GaN mesa with exposed N-layer; (d) GaN mesa after HF removing SiO₂; (e) Photolithography aligned metal contacts on GaN; (f) Light extraction testing on GaN LED.
In our LED devices fabrication, a SiO$_2$ layer was first PECVD-deposited and photolithography-patterned into squares of 350×350 μm$^2$ on GaN as the etching mask (Figure 6.8 a-b). Then GaN mesas were etched ~2 μm high by ICP (RIE-200iP, Samco) to form 350×350 μm$^2$ GaN mesas and expose N-GaN regions (Figure 6.8 c). After surface cleaning and SiO$_2$ stripping, Au/Ni (150/20 nm) and Al/Ti (200/20 nm) were deposited on the P-GaN mesas and N-GaN trenches by photolithography and lift-off, and annealed to form ohmic contacts to GaN (Figure 6.8 e).

6.4.2 GaN ICP etching

To make a LED, N-type GaN needs to be exposed for contact, meaning the optimized etching depth should be ~2 μm. Although both dry etching and wet etching of GaN (similar to sapphire etching, based on H$_2$SO$_4$ and H$_3$PO$_4$ acid) are possible, dry etching is preferred for patterning LED mesas, because: (1) dry etching offers steeper sidewall and better control of etching depth; (2) GaN layers include various chemical compositions (such as AlGaN, InGaN in the QWs), which may have distinct wet etching rates and thus cause poor etching control and rough sidewalls.

Since GaN is a chemically strongly bonded material and inert to most etchants [242], its ICP etching is typically done using chlorine based reactive gases such as Cl$_2$, BCl$_3$, and/or SiCl$_4$ mixed with Ar. Among the dry etching tools, ICP is a better choice than conventional RIE, as it decouples the ion bombardment energy (bias power) and ion plasma density (ICP power) and thus can achieve relatively low substrate damage and fast etching rates simultaneously.

Two different mask materials were tested for ICP etching, photoresist AZ 5214E (Figure 6.9) and PECVD SiO$_2$ (Figure 6.10).
First, 1.4 μm thick photoresist post-baked at 150°C for 5 min (Figure 6.9 a) was used for masking 4 min GaN etching (Cl₂:Ar = 25:5 sccm, ICP power 500 W, Bias power 100 W, 50 °C). Although the GaN etching depth was only ~1.1 μm (not sufficient), the photoresist was already badly bombarded and pin-holes were already formed in GaN under the resist (Figure 6.9 b), indicating the photoresist was not good to mask etching.
Figure 6.10 SEM images of ICP etching GaN using PECVD SiO$_2$ as the mask: (a) 800 nm thick SiO$_2$; (b) after 4 min etching at 150W bias power; (c) after 4 min etching at 200W bias power.
Another option was 800 nm thick SiO$_2$ deposited by PECVD and patterned by photolithography and RIE (CF$_4$:H$_2$ = 33:7 sccm, 50 mtorr, 300 W, 250 °C, 18 min) (Figure 6.10 a). Here relatively thick SiO$_2$ was used to ensure GaN was free from bombardment damage. With otherwise the same recipe (Cl$_2$:Ar = 25:5 sccm, ICP power 500 W, 50 °C, 4 min), the bias power was changed from 100 W to 150 W (Figure 6.10 b) and 200 W (Figure 6.10 c), and the corresponding etching depths in GaN were 1.3 μm and 2.1 μm, respectively. Clearly SiO$_2$ was able to safely mask Cl$_2$/Ar ICP etching, as SiO$_2$ is inert to Cl$_2$. The 200 W bias was ultimately used for GaN etching because it has a high etching rate (~0.52 μm/min) and good selectivity to SiO$_2$ mask (etching rate ratio GaN:SiO$_2$ = 11.1).

After ICP etching, the samples were all thoroughly degreased in warm acetone (~50 °C) for 15 min, oxygen plasma treated (10 sccm, 10 mtorr, 50 W) for 2 min, RCA1 cleaned for 15 min, BOE (1:6) dipped for 5 min (SiO$_2$ etching rate ~290 nm/min), and then RCA2 (HCl:H$_2$O$_2$:DI water = 1:1:5, 80 °C) cleaned for 15 min.

6.4.3 LED metal contact

The metal contacts to III-nitride materials are critical to achieving low series resistance for better performance [242]. Although N-type ohmic contacts can be easily formed by using Al/Ti as the contact metal [257], there are more concerns about the P-type contact [258, 259], because the GaN has a large bandgap (~3.5 eV) [241, 242] and thus high Schottky barriers for P-contact metals.

Al/Ti (200/20 nm) was e-beam evaporated on exposed N-GaN film as N-contact metal, and Au/Ni (150/20 nm) was deposited on the P-type GaN mesa as P-contact metal, with alignment gaps of 10 μm between the P-metal, GaN mesa, and the N-metal (Figure
The device underwent a rapid thermal annealing in forming gas (N$_2$/H$_2$ 6 slpm) at 450 °C for 2 min to achieve an ohmic contact to the N-metal.

![Figure 6.11 Aligned n-type (Al/Ti) and p-type (Au/Ni) metal contacts: (a) optical image; (b) side-view of SEM image.](image)

**Figure 6.11 Aligned n-type (Al/Ti) and p-type (Au/Ni) metal contacts: (a) optical image; (b) side-view of SEM image.**

Then the annealing conditions (gas flow, temperature, and duration) for P-metal was tested and optimized. It was found a relatively high temperature (i.e. >500 °C) with the oxygen presence was necessary to reduce the contact resistance, this is because both a high temperature and oxygen are required to form NiO, which is critical to lower the Schottky barrier to the P-GaN [260-263]. The formation of NiO can be evidently seen from the color change of the P-pad (Figure 6.12).
The same LED device before and after oxygen annealing was measured (HP semiconductor analyzer 4145B) on a probe station (Figure 6.13), showing clearly that the annealing reduced the resistance by nine orders of magnitude (current from pA to mA, Figure 6.13 a and c) and eventually led to the first successful LED device in our lab. At the same time, the interface of the P-metal and the P-GaN was improved (cross-sectional SEM images, Figure 6.13 b and d), with a sharp boundary (no interdiffusion and thus poor contact) before annealing and a blurred boundary (improved interdiffusion and better contact) afterwards. To further reduce the series resistance and lower the turn-on voltage, the device can be pre-annealed (~900ºC) before patterning metal contact pads to better activate the Mg-dopant in the P-layer [230, 239, 264].
Figure 6.13 LED devices before and after P-metal annealing. a-b, Before annealing: (a) poor I-V characteristics (with optical image of device as insert); (b) cross-sectional SEM view of as-deposited Au/Ni film showing clear interface to GaN (marked by arrow). c-d, After annealing in air: (c) I-V characteristics (with optical images of annealed device and lighting-emitting pictures as insert); (d) SEM of annealed Au/Ni film.

6.4.4 Improved light extraction on NPSS

Similarly, the GaN LED devices on NPSS substrates were also fabricated and characterized (Figure 6.14 a-c). The enhancement of LEE was observed from light output powers, which were collected by a detector through a lens. The LEDs on 200 nm pitch NPSS had a 70 % higher light output than those on the flat sapphire substrate, while the LEDs on 1 μm pitch NPSS was 40 % better (Figure 6.14 d).
The result clearly shows the advantage of sapphire nano-patterning in improving the performance of LED devices, and further performance improvement can be achieved by tuning the patterning pitch, height, and other parameters.

![Image](image.png)

**Figure 6.14 Improved LED light output on NPSS.** a-c, Optical micrograph of LED devices working at 1 mA injection current on: (a) non-patterned substrate, (b) 200 nm-pitch NPSS, and (c) 1 μm pitch NPSS. (d) The ratio of the light output power of 200 nm and 1 μm pitch NPSS LEDs to non-patterned LEDs. Image courtesy of Hao Chen.

### 6.5 Summary

In this chapter, a complete process for fabricating NPSS based GaN LEDs was described. For the first time in our lab, wafer scale (demonstrated 2") sapphire substrates were nano-patterned by NIL and wet etching, GaN was successful grown on depth-controlled NPSS substrates, a feasible fabrication process for blue GaN LED was
demonstrated with some critical issues (such as mask design, GaN ICP, metal contact annealing, etc.) resolved, and over 70 % light enhancement of NPSS was achieved.

The NIL-based NPSS technique has the advantages of low-cost and high-throughput, and can be directly incorporated into current LED industrial fabrication. To further improve the batch-to-batch device uniformity and performance, some fabrication parameters, e.g. nano-pattern geometry (size and pitch), sapphire wet etching depth control, GaN ICP etching recipe, P-metal annealing conditions, etc., must be optimized. The light extraction can be further enhanced by adding a current spreading layer and/or utilizing different packaging approaches (e.g. flip-chip [234]).
Chapter 7

Plasmonic Nano-bar Cavity Antenna Arrays for Ultrasensitive Infrared Molecule Detection

7.1 Introduction to infrared sensing

Infrared sensing is crucial to molecule detection, because many molecules have unique absorption fingerprints in infrared range that can be used for accurate molecule identification [265]. Compared to conventional infrared sensors [266, 267], plasmonic nano-sensors are less complex and more sensitive, and have been used for various molecules [268-271].

In plasmonic IR sensing, the key is to achieve enhanced infrared absorption, which increases the electric field experienced by the target molecules and results in better detection. Previously, periodic plasmonic nanoantenna arrays have been used for molecule detection [271-273], but they suffered from low absorption and thus a poor sensitivity (~1 % change in measured infrared spectra). On the other hand, a resonant cavity based plasmonic absorber has shown very high absorption (99 %) [274]; however, the cavity used for trapping light is fully enclosed in dielectric layers, and thus not
effective for molecule detection because no molecules can be deposited inside the cavity where the electric field is concentrated.

In this chapter, we present a new plasmonic structure based on a nano-bar cavity antenna array (proposed by Prof. Stephen Y. Chou), which features high absorption (~80% at ~3 μm), flexible wavelength tuning in mid-infrared (e.g. 1-5 μm), and high sensitivity (>10 times better than reported previously [271-273]). We also demonstrate a nanoimprint lithography (NIL) [40, 88] based approach to fabricate both the nano-bar imprint mold and the plasmonic structures without any electron-beam writing, providing a low-cost and high-throughput method for manufacturing infrared sensors.

7.2 Highly absorbing plasmonic nano-bar cavity antenna array

In our method, the high-absorbance periodic plasmonic structure consists of a transparent dielectric substrate (fused silica) with a patterned nano-bar pillar array, a thin metal (Au) bar on top of the fused silica pillars, and a thin metal film covering the space between pillars [54] (Figure 7.1 a). The above structure can be easily fabricated by metal evaporation on fused silica pillars, perfectly aligning the top metal disks to the bottom Au
back plane with a nano-gap (controlled by the pillar height and metal thickness). The Au evaporation also naturally forms a small overhang on the top disk and creates nano-dots on the pillar sidewalls, forming a vertical cavity between the top disk and bottom plane with small nano-dots in between. With excitation light polarized along the nano-bar long axis (Figure 7.1 b), the nano-gap cavity effectively localizes and enhances the electric field, which is further boosted by the Au nano-dots on the pillar sidewall, providing effective sensing of molecules.

7.3 Nano-bar mold fabrication

To fabricate the plasmonic structures, NIL was chosen over e-beam lithography (EBL), as NIL is a high-throughput method. The first step for NIL is to fabricate a large area imprint mold, which is achieved by a double-nanoimprint approach (also free from e-beam writing).

The approach is based on nanoimprinting two cycles of gratings and subsequent etching, with the second imprint orthogonal to the first, to form periodic bars with the length and width determined by the two sets of imprint, respectively (Figure 7.2). A tri-layer resist, consisting nanoimprint resist (NXR-1025)/ SiO2 (15 nm)/ crosslinked polymer ARC (typically used as anti-reflection coating, ~150 nm), was deposited on Si substrate. The tri-layer resist allows multi-step lithography on the same resist layer (ARC), because ARC is compatible with the resist/solvents in our method. The method also enables stacking of two or more sets of features to achieve desired nano-bars and other complex patterns by only liftoff and RIE. Since it does not require any wet etching, it is capable of defining the nano-features precisely without distortion. The tri-layer resist
is advantageous in its high aspect-ratios and steep side-walls as an etching mask, high etching selectivity to the underlying Si, and easy Cr liftoff, all of which are critical to fabrication of a nano-bar mold with excellent fidelity, uniformity and feature-size control.

Figure 7.2 Fabrication schematics of a nano-bar imprint mold. (a) Tri-layer resist (imprint resist/SiO₂/ARC) deposition on Si substrate. (b) 1st NIL and RIE top resist residual layer (to define bar length). (c) RIE mid-layer SiO₂ and stripping imprint resist. (d) Deposition of 2nd layer imprint resist and NIL (to define bar width). (e) Cr shadow evaporation. (f) Oxygen RIE of imprint resist and ARC, and stripping resist. (g) Cr evaporation and liftoff. (h) Si RIE and Cr etching.

In fabrication (Figure 7.2), the first grating was imprinted in NXR-1025 and transferred to the SiO₂ by subsequent O₂ RIE the residual resist (10 sccm, 2 mtorr, 50 W)
and O₂/CHF₃ RIE SiO₂ (1.5/10 sccm, 5 mtorr, 100W), followed by an acetone rinse to remove the resist (Figure 7.2 a-c). ARC was not etched in order to minimize the feature step difference in the following NIL. Then a new spin-coated NXR-1025 resist layer was nanoimprinted into gratings normal to the first SiO₂ grating, and capped with a thin Cr layer by a shadow evaporation (70º from surface normal, 2 nm each side) (Figure 7.2 d-e). The thin Cr cap provided a good protection to the following oxygen etching of resist to achieve a precise control of the nano-bar geometry. Then Cr/resist grating and the SiO₂ grating both masked following O₂ RIE of ARC, creating rectangular bar openings (Figure 7.2 f). The imprint resist was removed by an acetone rinse, reducing the mask height from ~400 nm (resist plus ARC) to ~150 nm (ARC) to minimize unwanted shadow effect and corresponding feature size variation in evaporation. Then Cr evaporation (15 nm) and liftoff (in RCA1 10 min) patterned Cr bars on Si (Figure 7.2 g). The Si bar mold (Figure 7.2 h) was finished by RIE Si for ~180 nm (O₂/CF₄/SF₆/Ar = 2/30/10/10 sccm, 300 W, 50 mtorr), removing Cr in CR-7 (Cyantek), cleaning in RCA1 (NH₄OH:H₂O₂: DI water = 1:1:5, 80 ºC), and vapor-phase treatment of mold release agent (MRA) (Nanonex NXT-110).

Specifically for infrared detection, we used two 950 nm pitch master grating molds (from Dr. Partick Murphy) in NIL, with grating widths of 700 nm (to determine bar length) and 200 nm (to determine bar width), respectively. The first grating mold patterned 250 nm wide SiO₂ gratings masks (Figure 7.3 b), and the second created 200 nm wide trenches in imprint resist (Figure 7.3 d), eventually forming nano-bars of 700 nm long and 200 nm wide (Figure 7.3 f and Figure 7.4).
Figure 7.3 Side-view (tilted 45º) SEM images of fabricated structures for a nano-bar mold. 
(a) As-imprinted tri-layer resist. (b) Imprinted second layer resist gratings (Cr coated) crossing SiO₂ gratings on top of ARC. (c) ARC nano-bar openings after oxygen RIE. (d) ARC nano-bar openings after stripping imprint resist (optional). (e) Cr nano-bars on Si after liftoff. (f) Si nano-bars after RIE and Cr etching.
Figure 7.4 SEM images of fabricated nano-bar mold: (a) a cross-sectional view; (b) a high-magnification top view; (c) a large-area top-view.

Since our processing is free of wet-etching, the fabricated nano-bars have straight line edges and sharp corners (Figure 7.4). These features lead to uniform lengths and widths of nano-bars over a wafer-scale, which are essential for uniform performance of the plasmonic nano-cavity antennas.
7.4 Infrared molecule sensor fabrication

Figure 7.5 Fabrication schematics of nano-bar cavity antenna arrays. (a) NIL using a nano-bar mold on fuse silica and oxygen RIE residual layer. (b) Cr nano-bar liftoff. (c) RIE and Cr etching to form fused nano-bars. (d) Au evaporation to create self-aligned nano-bar Au disks and Au back plane.

With the fabricated nano-bar mold, the plasmonic nano-bar arrays were fabricated using only three key steps: nanoimprint lithography to pattern Cr bars (Figure 7.5 a-b), etching the bar-shaped pillar array (Figure 7.5 c), and an Au evaporation (Figure 7.5 d).

The bar-mold was nanoimprinted (130°C, 5 min, 200 PSI) into ~190 nm resist (Nanonex NXR 1025) to pattern nano-bar openings with a minimal residual layer (~15 nm, Figure 7.6 a), and Cr bars were transferred onto fused silica substrate after a brief oxygen RIE (2 mtorr, 50 W, 1 min), e-beam evaporation, and liftoff in acetone (Figure 7.6 b). Then fused silica was etched by RIE (CF₄/H₂ = 33/7 sccm, 50 mtorr, 300 W) to achieve 70 nm high bar-shaped pillars, followed by etching Cr and RCA1 cleaning. The
fabricated nano-bars were slightly narrower (~185 nm, Figure 7.6 b), caused by non-vertical sidewalls of Si nano-bar mold (Figure 7.6 a) and slight size variation of the master grating mold. Then 50 nm thick Au was e-beam evaporated (0.4 Å/s, Temescal BJD-1800), creating 20 nm gap nano-bar cavity antenna arrays (Figure 7.6 c-d), formed by the top Au disks on fused silica bars and a back plane film. During the evaporation, Au self-assembled into nano-dots on the pillar sidewalls (Figure 7.6 d). Besides, Au deposited on the pillars dewet and expanded outward to form a ~15 nm overhang on the pillar perimeters. The Au nano-dots and the overhang further contributed to the localization of electric field between the disk and the bottom Au film.

Figure 7.6 SEM images of fabricated plasmonic nano-bar cavity antenna structures. (a) Imprinted bars in resist with a thin (~15 nm) residual layer (shown as insert). (b) Cr nano-bars after liftoff. c-d, Top-view and side-view (30° titled) of nano-bar cavity antenna arrays, with the insert cross-sectional view showing the bar width and the overhang.
The plasmonic cavity antennas were then measured in air using Fourier transform infrared spectroscopy (FTIR) (Figure 7.7a) (with the help of Yu Song and Prof. Claire Gmachl), with the polarization along the long-axis of the nano-bars. The measurements show the structures had a very high absorption (unity deducted by transmission and reflection) of ~78% (at 3.11 μm, or ~3220 cm⁻¹). Compared to previously reported plasmonic single Au-bars (10% at 3.6 μm [272]) or bar arrays (~30% at 1.7 μm [273]), our result showed much higher absorption, owing to our highly effective electric field localizing mechanism. The absorption can be further tuned by optimizing the cavity gap size and other geometric parameters.

To test how effective our structure is in molecule sensing, we self-assembled a monolayer of octadecanethiol (ODT, CH₃(CH₂)₁₆CH₂SH, Sigma-Aldrich) on the sample. This was achieved by a 24-hour soak in 1 mM ODT in ethanol, followed by a thorough rinse with ethanol. We then remeasured the FTIR spectra (Figure 7.7b), and found the monolayer ODT shifted the absorption peak by ~0.2 μm (or ~200 cm⁻¹ in wavenumber) to 3.30 μm with a peak absorption of 72%, indicating the large sensitivity of the plasmonic structure in probing local electric field perturbation due to the molecule adsorption.

The ODT molecule features were clearly indentified by the asymmetric (~3.43 μm, or ~2915 cm⁻¹) and symmetric (~3.51 μm, ~2850 cm⁻¹) stretching modes of CH₂-bonds [265], displayed as the dips/spikes in the reflection/absorption spectra. Compared to single layer Au bars which yielded ~1% spectra change at 3.43 μm [272], our plasmonic cavity antenna array achieved ~12.5% change (in reflection), showing >10 times higher sensitivity.
Figure 7.7 FTIR spectra of plasmonic nano-bar cavity antenna structures: (a) as-fabricated; (b) with a self-assembled monolayer of ODT (absorption of as-fabricated structure shown as dot line for comparison). Data curtsey of Qi Zhang and Yu Song.
7.5 Performance of plasmonic nano-bar cavity antenna array

To understand the mechanism of high-absorption and high sensitivity of our plasmonic structures and to derive an optimized design protocol, we performed a finite-difference-time-domain (FDTD) analysis (Lumerical, Inc.) on the plasmonic nano-bar cavity antenna. In the simulation, the structure periodicity (950 nm in both X and Y directions) allowed us to reduce the model to a single 3D cell, consisting of a fused silica (SiO$_2$) substrate with nano-bars (70 nm high, 700 nm long, and 185 nm wide), an Au bar disk (50 nm high, with 15 nm overhang), a 5 nm diameter Au nano-dot on the pillar sidewall, and a 50 nm thick Au back plane covering the rest of the substrate.

Figure 7.8 Simulated electric field distribution of a nano-bar cavity antenna structure in X-Z plane (Y = 0). Z-direction incidence, X-direction polarization.
Assuming normal incidence light with the polarization along the X direction, the electric field was calculated in the X-Z plane (at Y = 0, the bar symmetry plane) (Figure 7.8) at FDTD calculated resonance frequency (~3.19 μm, very close to experimental value 3.11 μm). The result showed strong localization and more than 4 orders of magnitude enhanced electric field.

For the best sensitivity design, the resonance of the nano-bar cavity antenna arrays need to match the target molecule vibrational wavelength, which is 3.4-3.5 μm for ODT in our study. This can be achieved by tuning the structure’s geometrical parameters, including the nano-bar length and width, the nano-cavity gap size, and etc. The effects of the length and width on the structure performance, i.e. the resonance wavelength λ, the line width FWHM, and the Q-factor (λ/FWHM), were calculated with the nano-gap as 20 nm (Figure 7.9).

With the nano-bar width fixed at 200 nm, the change in the bar length from 200 to 900 nm red-shifts the resonance wavelength from 1.5 μm to 4.8 μm (Figure 7.9 a-b), covering a wide range in near- and mid-infrared. The sharp dips/spikes at 1.18 μm on the reflection/absorption spectra (plotted for shorter bars only for display clarity) correspond to propagating surface plasmon on the Au backplane, which is not of interest in our application for molecule detection using localized enhanced field. If we fix the nano-bar length at 700 nm but change the width from 100 to 600 nm, the wavelength red-shifts (Figure 7.9 c-d) from 3.0 μm to 4.5 μm, the peak absorption decreases (due to enhanced transmission at the edge area), and the resonance width broadens (i.e. larger full-width half maximum, FWHM).
Figure 7.9 Simulated performance of plasmonic nano-bar cavity antenna structures. a-b, Spectra with different bar lengths (bar width 200 nm): (a) reflection (solid line) and transmission spectra (dot line); (b) absorption spectra. c-d, Spectra with different bar widths (bar length 700 nm). e-f, Resonance wavelengths, FWHMs, and Q-factors by tuning: (e) lengths and (f) widths, respectively.
The linear dependence of resonance wavelength on bar geometries allows flexible tuning of the wavelength by changing either the bar length or the width. For our cases, where highly selective (narrow FWHM) and highly sensitive detection (higher absorption) are needed, it is desirable to have relatively narrow bars (~185 nm in our experiment). The bar length is more preferably used for the tuning, because it yields a larger tunability (larger wavelength slope, i.e. 3.6 nm/nm in Figure 7.9 e, higher than 3.0 nm/nm in Figure 7.9 f for width tuning), more stable FWHM (smaller linewidth broadening), and a higher Q-factor (~10). In our experiment, the bar length was chosen to be ~700 nm to match the stretching modes of ODT molecules (~3.4 μm).

### 7.6 Other nano-bar structures

From the simulation results, we can see that it is very convenient to tune the performance of the plasmonic antennas by simply changing the nano-bar lengths and widths. This can be easily controlled by either choosing different grating molds for imprint or tuning the grating line width using other techniques. Using the same nano-bar fabrication method discussed above, we also fabricated different nano-bar molds with various feature sizes.

The first one has the same pitch (950 nm) as the previous one (Figure 7.4), the same length (~700 nm) but a different width (~530 nm) (Figure 7.10). This was achieved simply by using a mold with wider gratings in the second imprint cycle. Clearly the fabricated nano-bars had large-scale uniformity (Figure 7.10 c). According to the simulation, plasmonic cavity antenna arrays with such parameters should have a
resonance peak around ~4.2 μm and a broader resonance linewidth (~1 μm), making it suitable for detecting different molecules over a relatively larger wavelength range.

Figure 7.10 SEM images of nano bars of a 950 nm pitch, 700 nm length and 530 nm width: (a) side-view, (b) high magnification top-view, and (c) large area top-view.

The nano-bar fabrication method can also be used with two gratings of different pitches. For example, by first patterning a 950 nm pitch grating and then imprinting a 200 nm pitch grating, we achieved denser (~5 times) and narrower (width ~75 nm) nano-bar arrays over a large scale (Figure 7.11). These denser and narrower nano-bar structures are
expected to have an even more sensitive and selective response in infrared molecule detection.

![Figure 7.11 SEM images of nano-bars of a 950/200 nm pitch (X-Y axes), 560 nm length, and 75 nm width: (a) side-view, (b) high magnification top-view, and (c) large area top-view.](image)

Even smaller nano-bar structures were fabricated using 200 nm pitch gratings (Figure 7.12). The fabricated nano-bars were 180 nm long, 34 nm wide, and 20 nm away from each other. This nano-bar structure could possibly be used for sensing and other applications in the visible range, instead of infrared.
7.7 Summary

In this chapter, we demonstrate a plasmonic structure for high-absorbance and high-sensitivity infrared molecule sensing, achieving a >10 fold increase in detection sensitivity compared to single metal bars. The plasmonic nano-bar cavity antenna arrays can be realized using very simple fabrication (NIL, etching, and metal deposition) without any e-beam writing, making it suitable for high-throughput production. The
nano-bar NIL mold can be created by a novel method based on two-cycle nanoimprint on a tri-layer structure, which allows stacking two or more sets of nano-patterns (gratings and others) into one single complex structure. The method can be expanded to fabricate nano-bars of different lengths/widths/periods (e.g. from sub-100 nanometers to tens of micrometers) on the same substrate, thus allowing fast and accurate detection of multiple molecules. This method can be also used for fabricating more complicated structures, such as bow-tie antennas (by aligning gratings with an angle to each other in NIL) and split-rings, thus enabling many other optical applications, including meta-materials [275, 276] and optical circuits.
Chapter 8

Nano-fluidics for DNA Manipulation and Detection

8.1 Introduction to nano-fluidics

Advancement of micro- and nano-fabrication technologies has enabled the development of micro- and nano-fluidic systems [277, 278], which have been widely used for sorting [279-284], sensing [285, 286], and analysis [287, 288] of various biomolecules, e.g. cells [282, 288, 289], proteins [283, 290], and DNA (deoxyribonucleic acid) [55-57, 59, 283, 287, 291-293]. Among these molecules, research is intensely focused on DNA, because understanding the genetic information encoded in DNA molecules has huge potential benefits for fighting diseases and improving human health. Nano-confinement structures [287, 292, 293], such as nano-pores [294-298] and nano-channels [55-57, 59, 291], have emerged as perfect candidates for the next-generation sequencing tools, as they allow precise and fast manipulation, linearization, and detection of DNA molecules using optical and electrical approaches.

Compared to nano-pores, nano-channels can provide better DNA confinement and linearization, more uniform and stable fluidic environment, and thus in principle more constant DNA translocation speed. Nanoimprint lithography (NIL) has been adopted to
fabricate various nano-channel fluidic systems [55-57, 59, 291] in our lab under Prof. Stephen Y. Chou’s guidance, as NIL provides fast, reliable, and repeatable patterning.

In this chapter, fabrication techniques of multi- and single-channel based nano-fluidic systems are presented, and the DNA flow and manipulation in nano-channels are characterized. The understanding of the DNA flow behaviors in nano-scale will serve as the foundation for ultimately fabricating reliable nanogap detectors inside nano-channel for future DNA sequencing [59], which clearly requires more extensive studies than what is demonstrated in this chapter.

8.2 Fabrication of 70 nm wide multi-channel nano-fluidic devices

In this section, 70 nm wide multi-channel nano-fluidic devices are fabricated, and the DNA flow through the devices is discussed.

8.2.1 Fabrication process

The fabrication of a multi-channel nano-fluidic device (Figure 8.1) includes several key steps: nanoimprint lithography with a master grating mold, photolithography to define the micro-channel, access hole drilling, and device cleaning and bonding.

First, a 4” fused silica substrate was RCA-1 cleaned (NH₄OH:H₂O₂:deionized water = 1:1:5, 80°C), and thermally imprinted (resist NXR-1025) with a master grating mold of 200 nm pitch and ~130 nm width (Figure 8.1 a-b). Then 10 nm thick Cr lines were patterned on fused silica by capping the resist grating with Cr through a bi-directional shadow evaporation, oxygen RIE the residual resist, e-beam normal evaporation of Cr, and liftoff (Figure 8.1 c). The 4” fused silica wafer was then coated with a photoresist protection layer, diced into 1” squares, and solvent-cleaned.
Figure 8.1 Schematics of fabricating multi-channel nano-fluidic devices. (a) Cleaned fused silica substrate. (b) Imprinted nano-gratings in resist. (c) Cr nano-lines on fused silica by lift-off. (d) Photolithography patterned nano-fluidic window. (e) Etched nano-channels in fused silica. (f) Photolithography patterned micro-channels and reservoirs. (g) Nano-fluidic channels with aligned micro-channels. (h) DNA flow in nano-channels from access holes on the back of the sealed device.
Then the diced 1” fused silica chip was patterned by photolithography to define a nano-fluidic window (Figure 8.1 d). A CF₄/H₂ RIE (33/7 sccm, 300 W, 50 mtorr) etched into fused silica for about ~120 nm with the Cr lines and photoresist as the mask, forming 70 nm wide nano-channels in the photolithography- patterned window (Figure 8.1 e). Following that, the fused silica chip was cleaned by oxygen plasma, solvent, and RCA1, and patterned by a second photolithography and CF₄/H₂ RIE to define ~800 nm deep micro-channels and reservoirs aligned to the nano-channels (Figure 8.1 f-g).

The fused silica chip was then solvent-cleaned to remove the photoresist, coated with a new protective photoresist layer, attached to a copper block with the micro-reservoirs on the chip aligned to holes (~1 mm diameter) on the copper block, and drilled through the copper block with a sandblaster to form access holes. After drilling, the fabricated fluidic device was carefully cleaned by rinsing off the photoresist and sand particles with IPA (isopropyl alcohol), soaking in 1:1 mixed H₂SO₄ and H₂O₂ at 100 ºC for 20 min, and rinsing in DI water. Finally the device was bonded to a flat fused silica cover slip (22×22 mm², 0.17 mm thick), which was pre-cleaned in mixed H₂SO₄ and H₂O₂, by annealing at 1000 ºC for 1 hour (Figure 8.1 h).

8.2.2 Fabricated 70 nm wide fluidic channels

Using the above process, a fluidic device was fabricated (Figure 8.2) with a 200 μm long and 40 μm wide nano-channel region, which corresponds to 20,000 nano-channels, showing the high-throughput advantage of NIL patterning. The optical image (Figure 8.2 c) showed perfect sealing of the whole device without any air bubbles, and cross-sectional SEM image (Figure 8.2 d) after the direct bonding [103, 299, 300] showed 70 nm wide enclosed fluidic channels. The photolithography patterning allows easy tuning
of the length and the number of nano-channels by simply changing the nano-patterning window size (Figure 8.3), enabling systematic studies of fluidic behaviors. Nanoimprint defects, which have a clear optical contrast to show the channel direction, can be used for aligning the nano-channels parallel to the pattern window with a \(<3^\circ\) error.

Figure 8.2 Fabricated 70 nm wide nano-fluidic channels. a-b. Top-view SEM images of an unsealed device showing the overall alignment and the nanochannel interface. (c) Optical image of a sealed device. (d) Cross-sectional SEM image of the sealed nano-channels.

Figure 8.3 Nano-fluidic channels with different nano-pattern window sizes (before sealing): (a) 90 × 80 μm². (b) 90 × 40 μm².
8.2.3 DNA flow in 70 nm wide fluidic channels

After wafer bonding, the nano-channel device was mounted onto a home-made fluidic jig to test the DNA flow. The device was wetted by first pumping 0.5X TBE buffer (44.5 mM Tris and Boric acid, and 10 mM EDTA) with 0.1 wt % POP6 (Applied Biosystems, CA) through the nano-channels at 18 inHg (~9 PSI) overnight, and then by electro-wetting at 50V for 2 hours to completely drive out any air bubbles trapped in the micro-channels.

Then 30 μL DNA-containing 0.5X TBE buffer was prepared and loaded into the reservoirs, including 50 pg/μL lambda DNA (New England Biolabs Inc.) 5:1 labeled by YOYO-1 fluorescence dyes [301] (Invitrogen Corp.), an oxygen scavenging system (3% β-mercaptoethanol, 4 mg/mL β-D-glucose, 0.2 mg/mL glucose oxidase, and 0.04 mg/mL catalase), and 10 mM anti-bleaching dithiothreitol (DTT). Electrophoresis was used to drive the DNA molecules flow from the micro-channels into the nano-channels, with an applied electric field of $2.5 \times 10^3$ V/cm in nano-channels. Clearly shown from the

![Figure 8.4 Fluorescence images of λ-DNA flow in 70 nm wide nano-channels.](image)
fluorescence images recorded by an Andor Ixon3 EMCCD camera (electron multiplying charge coupled device, Andor Technology) through a 100X oil-immersed objective lens (NA 1.4), λ-DNA remained coiled in the micro-channels but stretched when it moved into the nano-channels (Figure 8.4 a), and were confined successfully to the patterned nano-fluidic window without any leakage (Figure 8.4 b).

8.3 Fabrication of 18 nm wide multi-channel nano-fluidic devices

Stretching long DNA molecules, which is key to DNA sequencing, can be realized by flowing DNA molecules in confined nano-channels [55]. The length of stretched DNA depends on the size of the nano-channels, and approaches the full contour length in channels smaller than 30-40 nm [55]. In this section, 18 nm wide nano-channels were fabricated by nanoimprint lithography and used for DNA stretching tests.

8.3.1 Fabrication process

First, 18 nm wide nano-channels were fabricated on a 4” fused silica wafer using NIL and a two-step feature size reduction technique, combining a tri-layer resist structure (section 2.3.2) and a bi-directional shadow evaporation (section 4.3.3).

Then two pieces of 1” square devices were diced from the 4” wafer with 18 nm wide channels, and photolithography-patterned with micro-channels. The first device was etched using CF₄/H₂ RIE to pattern the micro-channels and reservoirs 750 nm deep, and the second device was etched step-wise in different regions to achieve micro-channels that were 150 nm deep and 200 μm long near the nano-channel interface but 750 nm deep away from the interface.
Figure 8.5 SEM images of fabricated 18 nm wide nano-channels interfacing the micro-channel of different depths: (a) device #1, 750 nm deep; (b) device #2, 150 nm deep.

Both devices were baked at 110°C for 10 min before RIE to reflow the photoresist. The reflow caused a slope in the photoresist and thus led to the formation of a gradient profile in etched fused silica near micro-/nano-channel interface, which facilitated DNA flow into the nano-channels [291]. The gradient was evident for the first device (Figure 8.5 a) but less clear for the second one (Figure 8.5 b), because much longer (12 min
more) etching for the first one in fact further reflowed the photoresist during RIE. The two devices were then both thoroughly cleaned, bonded to fused silica coverslips, and examined by a 100X oil-immersion objective (Figure 8.6).

Figure 8.6 Optical images of nano-fluidic channels connecting to micro-channels of a depth of: (a) device #1, 750 nm; (b) device #2, 150 nm.

8.3.2 Electric field in nano-fluidic systems

![Figure 8.7 A schematic of nanofluidic devices with different channel dimensions in micro- and nano-patterned regions for evaluation of voltage and field distributions.](image)

Figure 8.7 A schematic of nanofluidic devices with different channel dimensions in micro- and nano-patterned regions for evaluation of voltage and field distributions.
Electrophoresis has been widely used to drive, manipulate and separate DNA molecules in micro-/nano-fluidic systems [302-305]. To understand how DNA flows in nano-fluidic systems, it is necessary to evaluate the voltage and electric field distributions. Typically a nano-fluidic system consists of differently functionalized regions with distinct dimensions, from macro- to micro- and further to nano-scale in reservoirs, micro-channels, and nano-channels (Figure 8.7). Therefore, tuning the geometrical dimension would affect directly the electrical properties in nano-channels. For example, assuming the buffer resistivity $\rho$ and current $I$ are consistent in fluidics, the voltage drops in nano-channels can be calculated by equations (8.1 – 8.3).

$$\frac{V_2}{V_1} = \frac{I \cdot R_2}{I \cdot R_1} = \frac{\rho \frac{L_2}{d_2 \cdot \eta_2 W_2}}{\frac{L_1}{d_1 \cdot \eta_1 W_1}} = \frac{d_1 W_1 / L_1 \cdot \eta_1}{d_2 W_2 / L_2 \cdot \eta_2}$$ (8.1)

$$V = V_1 + 2V_2 + 2V_3$$ (8.2)

$$V_1 = V / (1 + 2 \frac{d_1 W_1 / L_1 \cdot \eta_1}{d_2 W_2 / L_2 \cdot \eta_2} + 2 \frac{d_1 W_1 / L_1 \cdot \eta_1}{d_3 W_3 / L_3 \cdot \eta_3})$$ (8.3)

Here $d$, $W$, and $L$ refer to the depth, width, and length of the channels in different regions. $\eta$ is the filling factor indicating the amount of the channel area contributing to buffer conduction, which is ~0.1 for 18 nm wide 200 nm period nano-channels and ~0.5 for micro-channels with one half area occupied by patterned-pillars (Figure 8.6).

Therefore, the electric fields can be calculated in different channel regions, with their ratios determined only by $d$, $W$, and $\eta$ (equation 8.4).

$$\frac{E_2}{E_1} = \frac{V_2}{V_1} = \frac{d_1 W_1 \cdot \eta_1}{d_2 W_2 \cdot \eta_2}$$ (8.4)
Table 8.1 Calculation of voltage and field distributions in micro- and nano-channels.

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<td>150</td>
<td>100</td>
<td>5000</td>
<td>750</td>
<td>395</td>
<td>0.62</td>
<td>0.12</td>
<td>1.6</td>
<td>4.9</td>
<td>24.3</td>
</tr>
</tbody>
</table>

Sample #1: 750 nm etched micro-channel; Sample #2: step-wise etched micro-channel.

Using the experimental geometric parameters (Table 8.1), we can calculate the voltage and electric field distributions for both 18 nm nano-fluidic devices under a same external supply of 60 V. For both devices, most of the voltage would be dropped on the long micro-channels connecting to the reservoirs, and only ~2V and thus an electric field of 400-500 V/cm would be applied to the nano-channels. The only geometric difference of the two devices, the depth $d_1$ and $d_2$, does not significantly affect voltage and field inside the nano-channels, but greatly changes their values in the portion of the micro-channels near the nano-channel interface, making them 5 times larger for shallowly etched device #2 compared to device #1.

Therefore, the stepwise etching approach allows sufficient depth in micro-reservoirs and reservoir-connecting micro-channels for easy device wetting, while at the same time creating a shallow channel interface, which can better guide DNA flow into and out of nano-scale confinement (Figure 8.8). First, the shallow micro-channel regions have a depth smaller than the size of coiled $\lambda$-DNA (the radius of gyration, $R_g \sim 0.73$ μm [306]), thus acting as nano-slits to pre-stretch the DNA molecules, which would then experience a lowered entropic barrier to flowing into the nano-channels. Second, the enhanced field in these interface regions exerts a larger electrophoretic force on the DNA molecules to
drive them in and out of the nano-channels, hence reducing the clogging of DNA molecules at the entrances to and immediately inside of the nano-channels.

![Figure 8.8 Schematics of DNA flow in nano-fluidic channels connecting to micro-channels with: (a) an abrupt interface; (b) a gradually stepped interface. Red arrows show the electrophoretic forces applied on DNA molecules.]

8.3.3 DNA flow in 18 nm wide nano-fluidic channels

To compare the performance of the two devices, both were wetted with 0.5X TBE buffer, loaded with 50 pg/μL lambda DNA, and driven electrophoretically at 60V. From the fluorescence image (Figure 8.9) of device #1 (750 nm deep micro-channels at
interface), λ-DNA molecules were clearly able to stretch and flow into the 18 nm wide nano-channels.

![Figure 8.9](image.png)

**Figure 8.9 Fluorescence image of λ-DNA flow in 18 nm wide nano-channels interfacing 750 nm deep micro-channels.** The cyan dash lines indicate the interfaces of micro- and nano-channels.

However, DNA molecules were found to clog the nano-channel entrances, due to a high entropic barrier for the large λ DNA (contour length ~22 μm after staining [306]) to linearize and get into the 18 × 60 nm openings. Moreover, DNA molecules were also trapped in the nano-channels for a long time (>5 minutes during observation), acting as bright fluorescence noise stripes, which make the detection of useful single DNA events much more difficult. The DNA trapping in the nano-channels can be attributed to a reduced electric field in the nano-channels, because the clogged DNA at the channel entrance may block ionic flow to significantly increase the resistance at the entrance region, thus decreasing the voltage drop inside the channels.
Figure 8.10 Fluorescence images of λ-DNA flow in 18 nm wide, 60 nm deep nano-channels interfacing 150 nm deep micro-channels. The white dash lines indicate the interfaces of nano-channels and micro-channels. The white, red, and yellow arrows indicate the locations of three DNA molecules with an upward applied electric field. The scale bars are 10 μm.
In comparison, the second device with stepwise etched channels allowed the passage of DNA molecules much more smoothly. From the consecutively taken fluorescence images (Figure 8.10, 0.2 second exposure time each), we can clearly identify multiple DNA flow events driven by the upward-pointing electric field. At the recording time (t = 0 sec, Figure 8.10 a), DNA indicated by the white arrows had already passed through the nano-channels, and another two (marked by red and yellow arrows) had just arrived at the nano-channel entrance. The DNA molecules in the shallowly etched micro-channels were stretched to about 6-7 μm (~30 % of stained contour length [306-308]), whether entering or leaving the nano-channels, as they are confined to a channel vertically much smaller than their radius of gyration (0.73 μm [306]).

By measuring the positions of yellow marked DNA in shallow micro-channels from different fluorescence images (Figure 8.10 a-i), we can directly estimate its flow speed as ~28 μm/sec and a mobility of 1.1×10⁻⁵ cm²/(V·sec). The same DNA passed through the 40 μm long nano-channel within 0.2 second (Figure 8.10 i), thus leading to an average speed in nano-channel as 200 μm/sec (or 2×10⁻² cm/sec), which corresponded to a mobility of 5.0 ×10⁻⁵ cm²/(V·sec).

Interestingly, the DNA marked with the red arrow entered the nano-channel at 0.2 second, but stayed in the nano-channel for about 1.8 second before exiting (Figure 8.10 k). When entering the nano-channel, the DNA stretched to ~12 μm (55 % stretching, Figure 8.10 b), then contracted to 3 μm (Figure 8.10 c-f), and then gradually extended to ~7 μm and stayed at that state for 0.6 sec (Figure 8.10 g-i) before finally exiting.

There are some possible reasons for the staged movement of the DNA molecules in the nano-channels, such as local differences in sidewall roughness, ionic concentration,
and electric field inside nano-channels, etc. Another probable reason is that DNA went through a series of folding and unfolding events within the nano-channels [309]. It is possible that the DNA molecules entered the nano-channel not end-first, but middle-first, and the polymer chain deformed in the channel to reduce its conformational free energy [309]. Depending on the degree of folding and other parameters, the time for the DNA molecules to fully unfold and move out varied from less than 1 second to tens of seconds or even longer in our experiment.

8.4 Fabrication of single-channel nano-fluidic devices

Compared to multi-channel nano-fluidic devices, single-channel devices [57, 59] are more advantageous for DNA sequencing, because they can simultaneously isolate, stretch, and detect single DNA molecules in pre-defined nano-confined areas. Using metallic nano-gap electrodes embedded in nano-channels, the ionic current change induced by DNA translocation can be effectively detected [59], potentially allowing ultra-fast DNA sequencing.

NIL allows fast and reproducible fabrication of such single-channel devices, but a critical step is to create a single-channel/grating mold. Using innovative techniques combining nanoimprint lithography, anisotropic Si etching, and edge lithography [57], the single nano-channel mold was fabricated over a 1” square Si (110) SOI wafer (Figure 8.11). The method was proposed by Prof. Stephen Y. Chou and has been carried out by Dr. Xiaogan Liang previously [57]. Similar approach have been used to fabricate a 5 µm pitch, 100 nm wide nano-grating mold, discussed in Chapter 2.
By changing the deposited Si$_3$N$_4$ thickness, nano-grating molds of different widths were fabricated (Figure 8.12). The patterns imprinted in UV resists show that both the 80 nm wide nano-channels (mold from Dr. Xiaogan Liang) and the 110 nm wide channels (mold newly fabricated) were smooth, which is critical to uniform DNA flow.
Figure 8.12 SEM images of imprinted single nano-channels in UV resists of different widths: a-b, 80 nm wide; c-d, 110 nm wide.

Using the imprinted UV resist mask (Figure 8.12 a-b), which consists of 70 nm NXR-2030 and 70 nm NXR-3022, nano-channels were transferred into the 1” square fused silica chip by RIE. First, a 1 min O$_2$/CHF$_3$ RIE (1/10 sccm, 100 W) and a 3 min O$_2$ RIE (10 sccm, 100 W) were used to etch through the residual resists (Figure 8.13 a), and then CF$_4$/H$_2$ RIE (33/7 sccm, 300 W) etched 70 nm into the fused silica. The fused silica chip was protected with Al foil to expose only the alignment marks, and etched for 200 nm by CF$_4$/H$_2$ RIE to enhance the optical contrast of the alignment marks. Finally the device was cleaned by solvents and RCA1 to remove the resists (Figure 8.13 b).
The nano-channels in fused silica were 90 nm wide (Figure 8.13), ~10 nm wider than the patterns in imprint resist, mainly due to channel broadening by resist over-etch. The fabricated 20 mm long single nano-channels were aligned to micro-channels with different shapes (e.g. triangular and rectangular) at the nano-channel interface, and patterned to the desired lengths (10-60 μm) by photolithography (Figure 8.14).
The single nano-channel devices were then sandblaster-drilled to define access holes, thoroughly cleaned in 1:1 mixed H$_2$SO$_4$ and H$_2$O$_2$ at 100 °C for 30 min, and bonded to a fused silica coverslip by direct fusion bonding at 1000 °C for 1 hour. The sealed devices were then wetted with 0.5X TBE buffer by subsequent pumping and electro-wetting, and loaded with 50 pg/μL lambda DNA 5:1 labeled by YOYO-1 dye mixed with an oxygen scavenging system and DTT (see section 8.2.3).
Figure 8.15 Optical image and fluorescence image of a single nano-channel device: (a) optical image; (b) fluorescence image showing a DNA molecule in channel.

After electrophoresis for 1 hour at 60 V, λ-DNA molecules were driven through the single channel, which was 40 μm long, 90 nm wide, and 75 nm deep (Figure 8.15). The DNA molecules stretched to ~16 μm in the nano-channel (Figure 8.15 b), corresponding to 73 % of its full contour length (~22 μm [306-308]) after being stained with YOYO-1 dye [301].

The manipulation of single DNA molecules in single nano-channels enables the future study of DNA behavior in nano-confinement, as well as electrical detection of long DNA molecules.

8.5 Summary

In this chapter, we present the fabrication of multi-channel and single-channel nano-fluidic systems, and the manipulation of DNA in such nano-channels. The multi-channel
system allows high-throughput DNA flow, sorting, and manipulation, while the single-channel system enables identification of single DNA molecules for genome sequencing. Nanoimprint lithography, in combination with film deposition and selective etching techniques, provided a fast and reproducible route to fabricate the fluidic devices, and will be expected to play a more important role in future bio-medicine related research areas.
Chapter 9

Enhanced Fluorescence Detection of DNA in Fluidics Using Integrated Plasmonic Nano-sensors

9.1 Introduction to fluorescence detection of molecules

Fluorescence, a photoluminescence process, refers to the emission of light of a longer wavelength than excitation when the excited fluorophore releases the energy to its ground state (Figure 9.1 a). Fluorescence has been widely used in many applications, including energy-efficient illumination [310], bio-medical imaging [311], molecule sorting [280, 312], DNA sequencing [313, 314], single molecule detection [315], just to name a few.

In bio-imaging and sensing applications, strong fluorescence signals are very desirable for high-sensitivity and reliable analysis. To enhance the fluorescence, plasmonic nano-structures have been studied and proved very effective, because they can increase the excitation rate of the fluorophores and at the same time can work as effective optical antennas to increase the quantum yield of the fluorophores for enhanced radiative emission [316-318] (Figure 9.1 b).
Figure 9.1 Diagrams of fluorescence enhancement by plasmonic structures: (a) fluorescence without plasmonic structures; (b) enhanced fluorophore excitation and radiative emission with plasmonic structures.

However, the previous demonstrations [319-325] have some limitations. First, they used isolated nanostructures without a coupling cavity to concentrate the electric field, hence limiting the enhancement to a relatively low value (<10) for fluorescence dyes with a moderate quantum-yield (0.2-0.3) [321, 323]. Second, the studies used only small proteins [322, 324, 325] and DNA (20 base-pair) [323] molecules, but did not provide information for much larger molecules. Third, the molecules were fixed to a substrate such as glass-slides [319-325] rather than flowing in a well sealed fluidic system, thus not suitable for many practical molecule imaging and detection applications which require real-time and high-throughput readout.
In this chapter, we present a method to integrate a highly effective plasmonic structure [54] into sealed fluidic channels, and demonstrate up to 30 times enhanced fluorescence of large molecules (λ-DNA, 46.5 kb) labeled with a high quantum yield dye (0.46) flowing through the nano-plasmonic structures.

9.2 Integration of plasmonic nano-sensors in fluidic systems

Although very desirable, the integration of metallic plasmonic structures into fluidics faces many challenges, for example: (1) difficulty in bonding due to surface roughness from metal nano-structures; (2) incompatibility of metallic nano-structures with the multi-step fabrication process of fluidic devices, which requires harsh cleaning and high-temperature bonding; (3) potential oxidation (for silver) and degradation (from electro-chemical reactions) of metallic nanostructures in fluidics. Here we demonstrate our solution to use self-aligned integration and a room-temperature direct bonding technique.

9.2.1 Fabrication process

To fabricate a fluidic device integrated with a highly effective plasmonic nano-structure, i.e. disk-coupled dots-on-pillar antenna-array (D2PA) [54], we used nano-imprint lithography (NIL) [40, 88] for high-throughput and uniform patterning and a novel composite mask to self-align the nano-patterns in channels (Figure 9.2). The composite mask uses three stacks, including bottom and middle stacks of SiO₂/ARC (a crosslinked polymer) layers and a top nanoimprint layer, to pattern the fluidic channel, nano-patterning window, and nano-plasmonic structures, respectively. A key fabrication novelty is that the two stacks of SiO₂/ARC layers were kept as a part of the final lift-off structure to selectively pattern nano-structures.
Figure 9.2 Schematics of patterning plasmonic Au D2PA array in fluidic channels. (a) Fused silica substrate coated with bottom stack of SiO₂/ARC; (b) Micro-fluidic channels defined in fused silica; (c) Coating middle stack of SiO₂/ARC; (d) Second photolithography and RIE to define the D2PA-patterning window in SiO₂ (middle stack); (e) Nano-holes UV-imprinted in resist; (f) Cr nano-dots patterned on fused silica after liftoff; (g) Nano-pillar etching in fused silica; (h) D2PA arrays after Au evaporation.
Specifically, the fabrication includes the following steps. First, 40 nm thick ARC (baked at 180°C for 30 min) and 15 nm e-beam evaporated SiO₂ were coated on a 1” square fused silica chip (Figure 9.2 a), and then patterned to form 120 nm deep fluidic channels in fused silica with self-aligned SiO₂/ARC bottom stack (Figure 9.2 b) by photolithography and RIE (10 sccm, 100 W CHF₃ for SiO₂ and fused silica, and 10 sccm, 50 W O₂ for ARC). After that, the middle stack of SiO₂/ARC (15/40 nm) was deposited (Figure 9.2 c), and patterned by another photolithography and RIE into rectangular windows (200 μm wide, 1 mm long) in SiO₂ (Figure 9.2 d). Then the chip was coated with a UV curable Si-free imprint resist (Nanonex NXR-2110, ~200 nm thick), and UV-imprinted (150 PSI, 20ºC, 4 min, UV illumination 5 sec) using a nano-pillar mold (115 nm size, 200 nm pitch) to create nano-hole masks in the resist (Figure 9.2 e). The low-viscosity UV resist was able to flow readily and fill the fluidic channels. Following that, the resist was covered with a Cr mask by a four-directional shadow evaporation, exposed to oxygen RIE to remove the residual layer, and evaporated with 15 nm Cr. A liftoff in RCA-1 (NH₃H₂O:H₂O₂:deionized water = 1:1:5, 80ºC) stripped all the three stack of masks and self-aligned the nano-Cr masks in the fluidic channels (Figure 9.2 f). Then a CHF₄/H₂ RIE patterned 60 nm high nano-pillars in the fluidic channels, and Cr was etched in CR-7 (Figure 9.2 g). Then the chip was patterned with 700 nm deep micro-channels and reservoirs by photolithography and CHF₄/H₂ RIE, drilled with access holes by a sandblaster, and thoroughly cleaned in solvent and H₂SO₄/H₂O₂ (1:1, 100ºC, 1 hour). Finally, photolithography, e-beam evaporation, and liftoff deposited 50 nm thick Au onto the nano-fused silica pillars, creating plasmonic D2PA antenna arrays in the fluidic channels.
Using NIL and self-alignment, we achieved large-area and uniform patterning of nano-pillars in designed fluidic channels (Figure 9.3). UV NIL was preferred than thermal NIL, because UV resist has a lower viscosity and allows easier resist filling on the pre-patterned non-flat substrate.

Figure 9.3 SEM images of fabricated nano-pillars in fluidic channels: (a) high-magnification image showing 60 nm high, 115 diameter square pillars; (b) nano-pillars selectively patterned in fluidic channels and self-aligned to channel edge.
9.2.2 Sealing of fluidic devices with plasmonic structures

To achieve a good device sealing, which is very important to the reliable molecule detection in fluidic systems, we improved the fabrication from the following four aspects.

![Figure 9.4 Optical images of nano-pillars and plasmonic D2PA structures fabricated in fluidic channels: (a) nano-pillars in fluidic channels; (b) Au D2PA structures.](image)

First, the surface roughness on the channel top surfaces was minimized in fabrication. This was achieved by self-aligned fabrication of nano-pillars inside channels (Figure 9.3).
and positioning the rough metal edges (caused by liftoff) of D2PA region a sufficient distance (25 μm) away from the channel edge (Figure 9.4).

Second, the geometrical parameters (Figure 9.5), including the fluidic channel depth \( d \), the pillar height \( h \), the gold thickness \( t \), and the coverslip gap \( w \), were designed to reliably seal the device as well as to optimize device performance. The depth \( d \) was chosen sufficiently large (\( d = h + t + w \)) to make the plasmonic structures all below the channel edge. Here \( h \) and \( t \) were designed from tuning D2PA resonance wavelength and optimizing electric field enhancement, and \( w \) was minimized to 10 nm to confine the DNA flow in vicinities of the D2PA antenna arrays.

**Figure 9.5 Geometrical control for reliable integration of D2PA structures into fluidic channels.** (a) Cr dots in a channel of a depth \( d \). (b) Sealed device with a channel depth \( d \), pillar height \( h \), Au thickness \( t \), and coverslip gap \( w \).
Third, the unwanted defects and debris during fabrication were minimized by careful surface protection and thorough cleaning techniques. For example, before drilling access holes the device was carefully protected by a thick photoresist (AZ 9260, ~15 μm) and then a blue tape (Semiconductor Equipment Corporation) so that only the access holes were uncovered, therefore eliminating sand debris on device surface which could cause a poor contact. Besides, the drilled device was cleaned before Au deposition by 1:1 mixed H₂SO₄/H₂O₂, which removed any deposited polymer and dust particles and also increased the silanol group (-SiOH) density on the surfaces to facilitate a better bonding.

Last, the ozone cleaning of the device after Au liftoff removed residue photoresist polymer and created a clean, hydrophilic, and silanol group terminated fused silica surface, which is ready to bond. Using ozone cleaning instead of acid or high-temperature treatment, we can guarantee the Au plasmonic nano-structures are free from degradation and allow the best D2PA performance.

With the above issues carefully addressed, the fluidic device was directly bonded at room temperature to a fused silica coverslip (0.17 μm thick, 24 × 24 mm²) pretreated by H₂SO₄/H₂O₂ and ozone. By gently pressing the two pieces together, an initial contact area was formed and immediately propagated to cover the whole 1” device within less than 1 second, without trapping appreciable air bubbles in the device center (Figure 9.6). The device was then stored overnight at room temperature before being used for fluidic test.

Room temperature direct wafer bonding is expected to yield a bonding strength of 0.1-0.2 J/m² [103, 300, 326], which although is much smaller than permanently bonding (~2 J/m²) using a high-temperature (>1000ºC) annealing but allows a sufficiently long testing time (>24 hours in our test) for reliable fluidic manipulation.
Figure 9.6 Optical images of room-temperature directly bonded fluidic device: (a) overall view; (b) aligned D2PA in fluidic channels.

9.2.3 Performance of D2PA antenna arrays

The plasmonic D2PA structure is a 3D antenna array [54] created by evaporating Au directly on nano-patterned fused silica pillars. The Au D2PA antenna arrays had a
enlarged diameter (~145 nm) compared to the fused silica pillars (115 nm), due to Au dewetting and diffusion on fused silica pillars during deposition, and uniformly covered the deposited areas (Figure 9.7 b).

Figure 9.7 SEM images of fabricated D2PA arrays: (a) high-magnification 45º side view of 145 nm diameter D2PA arrays with a vertical cavity gap of 10 nm. The cross-sectional view is shown as insert. (b) low-magnification top view to show large-area uniform D2PA patterning.

The Au deposition forms Au disks on top of fused silica pillars and also an Au back-plane covering the pillar feet and substrate. The Au disks and the Au back-plane form vertical cavities at the 10 nm gaps, where the electric field is greatly enhanced [54]. The
field concentration is further enhanced by the self-assembled Au nano-dots on pillar sidewalls (Figure 9.7 a insert) and also by the coupling of the vertical cavities with the lateral cavities formed by Au disks.

Figure 9.8 Measured optical spectra of D2PA plasmonic arrays: (a) Transmission, reflection, and absorption of D2PA arrays; (b) Absorption spectra of D2PA and Au film, and enhanced absorption by D2PA.
The reflection and transmission spectra of the D2PA sample (Figure 9.8 a) were measured by a confocal spectrometer (LabRAM ARAMIS, HORIBA), with the signals collected by an Olympus objective (50X, NA 0.75). The absorption was calculated as unity deducted by the reflection and transmission. Clearly the D2PA structures had a much higher absorption (70 %) compared to an Au film of the same thickness (18 %) at a resonance wavelength of ~548 nm (Figure 9.8 b). Such a short-wavelength resonance was attributed to the highly symmetric geometry of the D2PA disk dimensions [327]. When in resonance, the D2PA structures could collect half of the incident energy, as seen from the D2PA-enhanced absorption, i.e. the D2PA absorption minus the Au film absorption.

To better understand its performance, a D2PA structure was modeled by a finite-difference-time-domain (FDTD) software (Lumerical, Inc.), with its geometrical parameters the same as in the experiment (Figure 9.9). The geometric symmetry reduces the model to a 3D single cell of 200 nm pitch. A mesh size of 2 nm was used.

To find the resonance of such a structure, a plane wave (400-900 nm) of a normal incidence was used as the light source. The simulated optical spectra of the D2PA structures were found very similar to the experimental data (Figure 9.9), with a resonance peak (~558 nm) slightly different from the experimental value. This is probably due to non-uniform geometrical parameters in experiment caused by surface roughness and feature size variation. The high absorption (~80 %) at the resonance makes the D2PA structure very suitable for high-sensitivity molecule detection.
9.3 Real-time observation of DNA fluorescence enhancement in fluidics

After wafer bonding and overnight storage, the fluidic device was carefully mounted onto a home-made fluidic jig, which was used for loading running buffer and DNA and also connecting electrical supplies to the device. Then the device was loaded with 0.5X TBE buffer with 0.1 wt % POP6, electro-wetted at 10V for 8 hours to gently drive out all air bubbles in micro-channels, and then loaded with λ-DNA (48.5 kb, 16.5 μm) 5:1 labeled with POPO-3 fluorescence dye (534/570 nm, Invitrogen Corp.)[328], an oxygen scavenging system, and anti-bleaching dithiothreitol (more material details given in Chapter 8).
POPO-3 dye was used to label the DNA molecules because of the following reasons. First, it is a stable intercalating dye [301, 329, 330] with a high quantum yield (0.46), and has been widely used for bright and reliable DNA imaging. Second, it is non-fluorescent when not bonded to DNA but becomes >1000 times brighter when bonded [301], thus greatly reducing background noise and enhancing the sensitivity [329]. Thirdly, its absorption (~534 nm) well matches the resonance of the Au D2PA antenna arrays (~548 nm) in this study.

![Figure 9.10 Optical spectra of POPO-3 absorption and emission, D2PA absolute absorption and enhanced absorption, and excitation light.](image)

The measurements were performed on an inverted fluorescence microscope (Eclipse TE300, Nikon). The green emission line of the mercury lamp at 546 nm was used as the excitation source, because it closely matches the absorption of the fluorescence dye (534 nm) and the D2PA absorption peak (~548 nm) for the best performance (Figure 9.10).

DNA molecules were driven by electrophoresis to flow from the micro-reservoirs into the D2PA-integrated fluidic channels, with a 10V voltage and an electric field applied 45º to the fluidic channel. An oil immersion objective (100X, 1.4NA) was used for
concentrating the illuminating light onto the sample and collecting fluorescence signals. The fluorescence signals passed through a 555 nm dichromatic beam-splitter and a band-pass filter (590/60, Nikon) before being recorded by an Andor Ixon3 electron multiplying charge-coupled device (EMCCD) camera.

Figure 9.11 Optical and fluorescence images of DNA in micro-channels to show leak-free device performance. (a) Optical image. (b) Fluorescence image.

DNA molecules can be seen from the recorded fluorescence image (Figure 9.11) to accumulate at the edges of the fluidic channels as driven by the electric field, but no DNA fluorescence was observed outside of the fluidic channels, showing the device was well sealed. In fact, the room-temperature sealed device lasted for 24 hours without appreciable leakage, but it degraded faster afterwards and started to leak seriously 72 hours after wetting. After the testing, the device was removed from the jig, separated from the coverslip, rinsed thoroughly with solvents and DI water, and saved for future reuse.
For a direct observation of fluorescence enhancement by D2PA antenna arrays, the $\lambda$-DNA molecules were driven to flow across the boundary of D2PA and fused silica nanopillar regions (Figure 9.12). Multiple DNA events were captured consecutively with a duration of 0.3 second per frame. The DNA fluorescence signals were clearly brighter in the D2PA region, but weak and indistinguishable from the background noise in the nanopillar region (Figure 9.12). Besides, the DNA molecules in the D2PA regions also had different enhancement factors. For example, the white-marked DNA had about a doubled fluorescence intensity compared to the yellow-marked (Figure 9.12).

![Figure 9.12 Consecutive fluorescence images of $\lambda$-DNA flowing through D2PA structures in fluidic channels. The white and yellows indicate two different DNA molecules.](image-url)
To quantify the intensity distributions, a home-made Matlab code was used to analyze the histograms of the DNA intensities in the two regions. The average fluorescence enhancement was calculated from data in 100 frames by dividing the average DNA fluorescence intensity in the D2PA region to the reference, which is the average intensity in nano-pillar region in the same frames. In order to best distinguish DNA from the background in the two regions, a pixel was identified as DNA only when its fluorescence was brighter than the average by a threshold value. Using threshold values of 800 and 50 in D2PA and nano-pillar regions, respectively, the average DNA intensities were calculated as ~2100 and ~210 in the two regions, resulting in an average fluorescence enhancement factor of 10 (Figure 9.13 a). The calculated average intensities were in good agreement with the values probed directly from the image. With lower threshold values, e.g. 500 in D2PA region, the average intensity only reduces <15 %; however, a high percentage (30-40 %) of background pixels are taken into account, thus reducing the accuracy.

The maximum DNA fluorescence intensity in D2PA region was ~6000, corresponding to an enhancement factor of about 30 (Figure 9.13 b). Such a fluorescence enhancement of a large λ-DNA molecule (48.5 kb, contour length ~22 µm after staining [306], radius of gyration ~ 0.73 µm [306]) has not been previously reported.
Figure 9.13 Histograms of DNA fluorescence intensities in fluidic channels integrated with plasmonic D2PA nano-structures. (a) Intensities in D2PA region and fused silica pillar regions showing an average of 10X enhancement; (b) D2PA-enhanced DNA intensities with a maximum of 30X enhancement.

There are two key reasons for such a high fluorescence enhancement in our fluidic system: (1) the D2PA structures boosted electric field (as high as >2 orders of magnitude, FDTD simulation Figure 9.14) to excite more dye molecules as wells as reduced the fluorophore lifetime on the excited state, leading to more photo emission, and (2) the
large coiled DNA was stretched by the nano-structures (D2PA and nano-pillars) into linearized chains, which can get closer into vicinities of hot spots where the electric field is concentrated (Figure 9.15).

Figure 9.14 FDTD-simulated electric field distribution in a plasmonic D2PA structure. Excitation wavelength 546 nm, plane wave normal incidence. A 4 nm diameter Au dot was modelled in the gap on the right side to evaluate the field enhancement.

Figure 9.15 Schematics of simultaneous DNA stretching and fluorescence enhancement by plasmonic D2PA structures in fluidic channels. The round green dots indicate the hot-spots for strong fluorescence enhancement.
The D2PA structures have been demonstrated for its capabilities of greatly enhancing electric field and promoting molecule detection sensitivity [54] due to high electric enhancement and also high density of hot spots (25 D2PA antennas each $\mu m^2$). The hot spots, visualized from the FDTD-simulated field distribution (Figure 9.14), include the peripheral nano-gaps surrounding the Au disk antennas, where the field is highly enhanced (>200 times) and highly localized (~10 nm laterally), and also the edges of the Au disk antennas, where the field is moderately enhanced (>10 times) and less localized (effective ~20 nm laterally and ~40 nm vertically).

As DNA molecules move through the D2PA arrays in the fluidic channels, they are expected to be squeezed in the regions between adjacent D2PA antennas rather than in the 10 nm deep vertical slits between the antennas and the coverslip ceiling. This is because the vertical slits are so shallow that it requires a high degree of DNA linearization [55, 308], which is less energy-favorable. Also the fluidic velocities at the surfaces of coverslip and the D2PA top are close to zero, thus greatly limiting the flow speed in that slits.

When the $\lambda$-DNA molecules flow in between Au D2PA antennas, they can be effectively stretched [55, 308], as observed from the EMCCD-captured images (Figure 9.12). This is because the DNA size (0.73 $\mu m$) is much larger that of the nano-fluidic channels of that region in both the vertical dimension (~70 nm vertically from Au backplane to coverslip) and lateral dimension (60 nm between Au disks and 85 nm between pillars). The stretching also possibly enables the linearized 2 nm diameter DNA [293] to enter the D2PA nano-gaps where the electric field is the highest.
This nano-confined space in adjacent D2PA antennas also increased the chance of DNA to get close to the vicinities of the D2PA hot spots. Assuming a uniform spatial distribution in all the space, the chance is \( \sim 30\% \) to find the DNA around the Au antenna edges and \( \sim 6\% \) in the vertical cavity gap. The real probability for the DNA to squeeze into the 10 nm vertical gaps could be smaller, as the entropic barrier for DNA to flow in is expected high.

![Image of DNA fluorescence intensity](image)

**Figure 9.16 Average DNA fluorescence intensity of 50 consecutive images.**

The fluorescence images (Figure 9.12) showed that the intensities of a same DNA changed with its flow, with some pixels brighter than the others. And the fluctuation can be more evidently seen from the averaged fluorescence intensities of 50 consecutive images (Figure 9.16). The isolated bright spots in the D2PA region (Figure 9.16) clearly trace the DNA flow, but the DNA movement outside the D2PA region can not be resolved, indicating greatly enhanced detection of DNA by the D2PA plasmonic structures. The intensity fluctuation was probably caused by the spatial fluctuations of
DNA distance to the D2PA hot spots, as a result of the change in DNA speed, shape, and location during flow. To improve the DNA fluorescence, the D2PA geometries can be optimized to achieve a larger hot-spot occupied space and a better rate of fluorescence enhancement, e.g. by further reducing the gaps between the adjacent D2PA antennas. Since the plasmonic D2PA structures were high-density packed with a pitch of 200 nm, very close to the resolution of the EMCCD camera (~150 nm each pixel), we expect even higher and more continuous DNA fluorescence signals can be achieved by further optimization.

9.4 Summary

In this chapter, we present a systematic study of real-time enhanced DNA detection in fluidic systems integrated with Au plasmonic D2PA antenna arrays, which were patterned by nanoimprint lithography. The D2PA plasmonic arrays were designed to achieve successful device integration and high electric field enhancement. A novel fabrication method was developed to seal the fluidic device using self-aligned nanopatterning, improved device cleaning protocol, and a room-temperature direct wafer bonding technique. This method allows reliable sealing of the device for a sufficiently long time (24 hours) and repeatable device use. Large DNA molecules (λ-DNA) were labeled with a high quantum yield dye, POPO-3, and flowed into the fluidic systems. The D2PA arrays were identified effective in fluorescence, providing up to 30 times fluorescence enhancement and an average of 10 times. Our approach of integrating plasmonic structures in fluidics can be used for high-sensitivity molecule detection, DNA sequencing, and many bio-imaging applications.
Chapter 10

Conclusions

This dissertation has detailed nanoimprint lithography (NIL) based novel nano-patterning techniques for fabricating functional structures and devices, especially in the potential applications of advanced electronics and high-sensitivity molecule sensing.

NIL is a high-throughput, high-resolution, and low-cost patterning technique, capable of generating nano-scale features over wafer scale within minutes. For best performance of nano-scale devices, it is often desirable to customize the nano-structures to achieve reduced size, smoothened edge, large feature aspect-ratio, multi-stack integration, etc. To obtain the desired nano-features, it is necessary to combine other techniques with NIL. In this dissertation, some techniques have been exemplified, including shadow evaporation (Chapter 2 and 4), self-perfection by liquefaction (SPEL) (Chapter 3), tri-layer resist patterning (Chapters 2 and 7), KOH Si etching (Chapters 2 and 8), and self-aligned selective nano-fabrication (Chapter 9).

Nano-patterning is critical to advanced electronics, because it can boost the device speed, increase the packing density, and reduce the power consumption. Moreover, it also opens research opportunities for novel devices. In this dissertation, nano-structures for two different transistors, i.e. Si/SiGe heterojunction tunneling transistors (HETTs) and graphene nano-ribbon (GNR) transistors, have been prototyped in Chapter 4. A shadow
evaporation based method has been used to create as small as 10 nm trenches self-aligned to a gate, which solves one problem in HETT transistor fabrication of precisely aligning the SiGe source to the transistor gate. For fabricating high-performance graphene transistors with an opened bandgap, 20 nm wide GNR arrays have been transferred to SiO₂ by electrostatic exfoliation from a graphite stamp, which is NIL pre-patterned using a nano-trench mold made by gradual line-width shrinking.

Nano-science welcomes new physical phenomena. In nano-scale, the surface and/or interface in many aspects provide novel intriguing properties that can dominate the overall behavior of the structure or device. For instance, controlling Si nanowire growth on amorphous substrate is very challenging, because the substrate does not well fix the catalyst or guide the nanowire growth. This problem has been solved by using a nano-patterned multi-layer Si-mediated Au catalyst (Chapter 5) which, through a pre-growth annealing driven by surface/interface energy minimization, melts first into an AuSi alloy ball and then naturally cools into an Au particle and a Si shell. The obtained size-, location-, and crystallization-controlled Au particles and Si base layer have been used to grow straight and uniform nanowires on amorphous SiO₂.

In biology and medicine, micro- and nano-patterning techniques enable advanced studies of bio-molecules such as DNA, proteins, and cells. One spectacular observation is that coiled large DNA molecules can stretch themselves into long linear chains when they are confined in a nano-scale space, such as a nano-channel, because the linearized state is more energetically favorable. Based on this, multi-nanochannel and single-nanochannel fluidic devices have been fabricated to study the DNA flow behavior in the nano-
confinement and to explore the possibility of direct DNA sequencing using such a nano-configuration (Chapter 8).

Besides, nano-structures can significantly affect the performance of nano-optical devices with their features sizes comparable to or smaller than the light wavelength of interest. For example, nano-texturing sapphire substrates by NIL and anisotropic wet etching has been shown to improve the light extraction of GaN light emitting diode (LED) devices by 70% (Chapter 6).

Metallic plasmonic nano-structures, in particular, can be designed to interact with light to illustrate very interesting phenomena, such as negative refraction, extraordinary light transmission, highly localized and greatly enhanced electric field, etc. One plasmonic structure, disk-coupled dots-on-pillar antenna (D2PA), has been demonstrated to be very straightforward to fabricate but effective in enhancing the localized electric field and flexible in tuning the resonance wavelength. These properties have enabled a variety of nano-sensors, including surface-enhanced raman scattering (SERS) based molecule detectors, and, in chapter 7 of this dissertation, an infrared nano-bar shaped detector that has a >10 times higher sensitivity than previously documented similar plasmonic sensors.

For the best performance of functional nano-structures, it is often desirable to build an integrated system incorporating not only the nano-structures themselves but also the necessary supportive components for manipulation, detection, and analysis. In chapter 9 of this dissertation, plasmonic nano-sensors have been integrated into fluidic systems for simultaneous DNA stretching and enhanced fluorescence detection. The successful integration is based on understandings of multi-disciplinary fields, including NIL, self-
aligned patterning, wafer bonding, plasmonics, fluorescence detection, micro-/nano-fluidics, and DNA manipulation.

All in all, NIL based nano-fabrication enables a wide variety of new opportunities in nano-scientific research, from electronics to material science, nano-optics, and nanobiotechnology. This dissertation has detailed a few examples in different disciplines, hoping to provide some basic understanding for those who are fascinated by the nano-world.

Many techniques presented in this dissertation can be generalized to other related fields. For example, the nano-patterned host-mediated technique can be used for growth of other wires and patterning of other metallic particles for possible plasmonic applications, the fluidic systems can be integrated with more functionalities and used for detection of other molecules, the fabricated 5 μm pitch nano-pillar arrays can be utilized to study fascinating plasmonic behaviors of single D2PA antenna, just to name a few. The opportunities are always left to those who are most prepared and eager to explore the unknown.
Publications

Journal papers


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