FLEXIBLE POLYMER MOLD AND
UV-CURABLE MATERIALS FOR NANOIMPRINT
AND ADVANCED NANOFABRICATION

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A DISSERTATION
PRESENTED TO THE FACULTY
OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

RECOMMENDED FOR ACCEPTANCE BY
THE DEPARTMENT OF
ELECTRICAL ENGINEERING

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June 2018
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Abstract

As an emerging nanofabrication technique, nanoimprint lithography (NIL) has inspired and realized tremendous inventions of high-performance electronic, photonic, biological and nanodevices. However, challenges are still present in order to embrace NIL in a full-scale industrial production: (1) Large-area, high-throughput and cost-efficient master mold fabrication with novel patterns; (2) New mold architecture with balance of conformal contact and desired resolution; (3) Novel imprinting materials for temporal pattern transfer or direct utilization.

This work contributes several unique solutions: (1) By manipulating post-imprint Cr etching mask transfer (e.g., inversion, transformation and multiplication) with multi-layer material stack, shadowed film deposition and consecutive imprints, large-area (up to 4-inch wafer scale) SiO$_2$ master molds were built with new features (135 nm-pitch pillar array, 1 µm-pitch triangular pillar array and moiré pattern array) from simple 1D grating molds and thermal NILs. (2) Sub-30 nm resolution, 50 × 20 cm$^2$ PFPE-based flexible hybrid mold structures were proposed, demonstrated and applied to UV NIL with overlay alignment ability (< 0.12º orientation error), great fidelity (> 98.5%) and great potential in continuous roller UV NIL fabrication. (3) High-performance POSS UV NIL resist systems, featuring two polymerization mechanisms, ideal mechanical and chemical stability, and great etching selectivity to regular Si-type substrate materials. (4) Novel one-step transfer printing nanofabrication approach to deliver metallic thin-film nanostructures to patterned rigid substrates and extreme fragile and soft plastic films.
Acknowledgements

First, I shall give my great appreciation to my advisor, Professor Stephen Chou. As the inventor of nanoimprint lithography and its pathfinder in the past 20 years, Professor Chou and his vision, passion and motivation to purse better lead the Nanostructure Lab and push all of us to explore the beyond. In the recent world full of distractions, few people can own such determination and faith close to his strong resolution. His dignity to scientific research earned the entire group respects and recognitions around the world, and I’m very proud of being a member of it. As a student, I received tremendous priceless advices and encouragement from him to realize my shortcomings and to overcome my inside fear and hesitation, and his continuous and generous financial support helped me to go smoothly in my career.

I’m very lucky to have been working with members in the Nanostructure Lab, who are kind, smart, motivated and supportive, and my sincere thanks go to them: Dr. Chao Wang and Dr. Siran Li provided help in my very first project on mid-IR plasmonic absorber at Princeton. Dr. Weihua Zhang taught me FDTD simulations on general plasmonic structures, and Dr. Liangcheng Zhou offered tutorials on optical setups and in-lab instruments for optical characterizations. I received the lab training from Dr. Hao Chen, and worked with him closely in several successful projects later. I have joint force with Ruoming Peng and Yuxuan Wang on the fabrication of plasmonic color filter, in which they showed a great collaborative spirit. Dr. Wei Ding and Ji Qi gave many precise feedbacks on flexible mold applications in solar cell and OLED fabrication. Dr. Eric
Mills assisted me in lab managements and equipment troubleshooting in a professional way.

I greatly appreciate Professor Claire Gmachl and Professor Sigurd Wagner as my PhD general exam committee members and their meaningful advices. I sincerely thank Professor Nao Yao and Professor Claire Gmachl as my PhD dissertation readers and all inspiring comments, and thank Professor Gerard Wysocki and Professor Minjie Chen for joining the FPO as the committee members.

Many Princeton staff members in the department showed me desired help: Jessica Johnson and Sarah McGovern for administrative managements, Linda Dreher and Lidia Stokman for routine purchasing orders, Dr. Sen Liu and Joseph Palmer for facility trainings.

My faithful and supportive friends also made my life in Princeton more enjoyable and memorable: Dr. An Dai, Yaowen Yeh, Yanbing Liu, Sili Deng and Mingxuan Wu.

Finally, my deepest gratitude belongs to my family. Although I live so far away from home across 12 time zones, my parents’ love and support, just like their warm embrace, give me tremendous power to overcome obstacles and pursuit a brighter future for the family. Cui Huang, my lovely wife, accompanies me with her best age in the entire life, giving me inspiring suggestions, strong confidence and heroic courage. With true hearts to each other, even the 5-year long-distance relationship won’t stop us be blessed to form the family. I’ve got every aspect of support that my family can grant in the past 6 years, now it’s the time for me to repay them with my full capacity in everything.
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Chapter 1

Introduction

1.1 Nanofabrication

As the natural extension of microfabrication techniques [1-2], nanofabrication with high resolution [3-4] has drawn tremendous attention from both the academia and industry, when applications of advanced devices with nanometer-scale features proved superior performances in electrical, photonic and biological areas. The major challenge is to combine high-resolution, high-throughput, large-area and cost-efficient characteristics at the same time.

To realize high-resolution nanofabrication, the most conventional and straightforward approach is to promote and advance photolithography technique, which is originally widely used in mass microfabrication. Photolithography topologically structures a light-sensitive material, namely photoresist, by light-induced chemical modification through a master photomask. According to Rayleigh’s criterion, resolution of photolithography is limited due to light diffraction, and proportional to λ (light source wavelength) / NA (numerical apertures of lens). The industry has focused on decreasing the wavelength of the light source, increasing the numerical aperture of the lens (e.g., 193-nm ArF immersion technique [5]) and adopting other resolution-enhancing methods [6-9] for decades to achieve higher patterning resolution. The state-of-the-art pilot
photolithography in extreme UV (EUV) \(^{10-11}\) and X-ray \(^{12-13}\) ranges for 10-nm feature fabrication have been demonstrated \(^{14}\), but its commercialization is held back by the needs of powerful yet complex sub-systems for high vacuum and adequate EUV-light sources \(^{15}\). Beyond photolithography techniques, electron-beam (e-beam) lithography \(^{16-17}\) uses low De-Broglie wavelength of electrons by scanning a focused e-beam onto an electron-sensitive resist to realize maskless sub-10nm patterning \(^{18-19}\). However, the process in the current development phase is considerably slow and still not practical for mass productions \(^{20}\).

Beyond these conventional beam-based nanofabrication methods, many unconventional nanofabrication approaches have been proposed and demonstrated, which utilize either physical masking and contacting, or chemical modification and self-assembling as working principles. They all possess natural advantages due to their own unique procedures, but also associated with drawbacks: Dip-pen nanolithography \(^{21-23}\) is a scanning probe based nanofabrication method where an atomic force microscope (AFM) tip or a two-dimensional tip array is used to generate 10-nm resolution chemical material (e.g., alkane thiol, silane, protein, DNA and peptide) patterns \(^{24-27}\) in a serial manner, with high overlay accuracy, maskless direct-write, biocompatible and scalable properties. However, it is still relatively slow due to the serial process nature and limited application scenarios in chemical array formation. Soft lithography \(^{28-30}\) uses replicated flexible elastomer polydimethylsiloxane (PDMS) structures to carry out self-assembly based micro- and nanofabrication with a convenient, effective, and low-cost method. Although five related techniques have been demonstrated: microcontact printing (µCP) \(^{31}\), replica molding (REM) \(^{32}\), microtransfer molding (µTM) \(^{33}\), micromolding in capillaries
(MIMIC) \textsuperscript{[34]}, and solvent-assisted micromolding (SAMIM) \textsuperscript{[35]}, they all have the limited resolution down to 30 nm due to the low Young’s modulus of intrinsic PDMS material \textsuperscript{[36]}. Aluminum oxide (AAO) lithography \textsuperscript{[37-38]}, stencil lithography \textsuperscript{[39-40]} and nanosphere lithography \textsuperscript{[41-42]} all share the same working principle that uses physical shadow masks with nanometer-size apertures to fabricate patterns in a resist-less, simple, parallel process. However, these mask materials and structures are either for single-use only or require complicated cleaning procedure, making the entire fabrication inefficient and low-throughput. Directed self-assembly of block copolymer (DSA) \textsuperscript{[43-44]} is a promising strategy that segregates a hybrid polymeric network into a variety of ordered structures by the repulsion of the immiscible blocks in order to enable sub-20nm resolution nanofabrication \textsuperscript{[45]} with advantages of easy pattern density multiplication, high throughput, line edge roughness reduction and cost reduction. However, extra efforts are still needed to address the uniformity and defect control issues for large-area fabrication, and this technique requires conventional ArF lithography or e-beam lithography for better pattern geometry and orientation control \textsuperscript{[46]}.

Different from all of the previous nanofabrication concepts, nanoimprint lithography can combine all desired properties of large area, high resolution, high throughout and low cost, and therefore considered as the optimal candidate of next-generation nanofabrication.

1.2 Nanoimprint Lithography

Nanoimprint lithography was first invented by Professor Stephen Chou in 1996 \textsuperscript{[47-48]}, and overwhelmingly accepted and extensively studied by many researchers with diverse
designs and implementations in the past 20 years \cite{49-50}. Due its vast popularity and great potential for high resolution, high throughput and large area nanofabrication, the MIT Technology Review recognized NIL as one of ten emerging technologies that will strongly impact the world \cite{51}, and the International Technology Roadmap for Semiconductors (ITRS) promoted NIL into the map as a candidate 32 and 22 nm node IC production technology in 2003 \cite{52}. In 2007, Toshiba became the first industrial user to validate NIL for 22 nm and beyond \cite{53}. Nowadays, there are still major challenges for NIL to meet the strict demands of massive production of commercial IC devices, particularly in overlay accuracy \cite{54-55}, defect control \cite{56-57} and mold lifespan \cite{58-59}. However, NIL has found its advantageous applications in novel multidiscipline devices in electronics (e.g., room-temperature single-electron transistors \cite{60}, 60-nm transistors \cite{55}), photonics (e.g., infrared nano-rings resonators \cite{61}, solar blind UV filters \cite{62}, plasmonic antenna arrays \cite{63-64}, plasmonic nanocavity OLED \cite{65} and solar cell \cite{66}) and bio-sensing cases (e.g., fluidic nano-channels for DNA analysis \cite{67}, bumper array for biomaterial manipulation \cite{68}, and nano-gap detector for DNA sequencing \cite{69}).

As an unconventional nanofabrication approach, Nanoimprint lithography (NIL) creates patterns of imprint resist materials by direct mechanical deformation, when pressing a master mold under a certain working pressure, other than relying on energized photons or electrons to change the physical and chemical properties of the resist material, so NIL is able to deliver a higher resolution beyond the limitations from light diffraction or scattering induced from traditional lithography techniques \cite{70}. NIL is also a 1:1 high-fidelity pattern transfer process with patterned resist features completely complementary to those on the master mold, and large-area fabrication capability is also in great potential.
when adopting a full-wafer sized master [71-72], step-and-flash approach [73-74], or roller imprinting [75-76]. Based on different formation mechanisms, the imprint resist can be a monomer or polymer system which is capable of curing by heat or UV radiation during the imprinting, and the corresponding NIL approaches are named thermal NIL and UV NIL, respectively [77].

In a typical thermal NIL process (Figure 1.1a-d), a thin-layer resist of thermoplastic polymer solution is first spin-coated onto the target substrate, and placed into contact with the master mold with pre-patterned topological features. The entire assembly is pressed under a proper working pressure, and heated up above the glass transition temperature ($T_g$) of the resist polymer. With the help of elevated temperature beyond its $T_g$, the resist layer exhibits much lower Young’s modulus and viscosity so that the features on the master mold will be pressed into it. After being cooled down to room temperature in a controlled sequence, the master mold is carefully separated away, leaving complimentary resist patterns on the substrate with a minimized residue layer. A short-duration reactive ion-etching (RIE) process removes the residue layer, and other subsequent pattern transfer processes (e.g., Cr etching mask deposition) can be performed accordingly.

Different from thermal NIL, UV NIL (Figure 1.1e-h) uses a low-viscosity liquid-state resist at room temperature which can be rapidly polymerized into a firm solid state when exposed to intensive UV radiation. A transparent master mold typically made from fused silica substrate is used to provide a pathway for incident UV light. Due to the low-viscosity nature of the UV resist, a much lower working pressure is required to fill resist into recessed mold area at room temperature, and a very thin residue layer is generally
available after UV curing and mold separation. A similar RIE step can fully expose the substrate for post-NIL fabrication.

Figure 1.1 Key steps of nanoimprint lithography: (a-d) Thermal NIL, (e-h) UV NIL

To further advance NIL performances, several challenges must be faced and novel solutions have to be proposed:

1. NIL master mold features and materials. NIL is the high-fidelity transfer of master mold patterns so building master molds with novel features in a large-area, high-yield and low-cost way will be a critical task before any NIL fabrication can be performed. One promising solution is to use a generally simple pattern (e.g., gratings) as the basic building block and generate more complex features by manipulating successive etching
mask transfers (e.g., union, subtract \textsuperscript{[64]} and multiplication \textsuperscript{[78]}) during consecutive NILs. In such a way, the NIL advantages in simplicity, large area and high throughput can be maximized to create new master molds.

Mold material is another essential factor dominating NIL performances. Originally, rigid materials such as silicon, dielectrics (e.g., silicon dioxide and silicon nitride \textsuperscript{[79]}) and metals (e.g., nickel \textsuperscript{[80]}) were adopted due to high stiffness, strong mechanical strength and chemical stability to ensure sufficient feature resolution and mold durability. However, NIL with rigid molds generally requires a high working pressure more than 200 Psi to guarantee a conformal contact over large sample area, and mold surfaces have to be carefully modified with special releasing agents \textsuperscript{[58, 81]} with low surface energy prior to NIL, in order to facilitate the separation. These extra requirements increase NIL complexity and introduce mold lifespan issues resulting from process-induced physical damage \textsuperscript{[82-83]} and anti-adhesion coating degradation \textsuperscript{[84-85]}. Flexible NIL molds made of fluorinated polymers \textsuperscript{[86-88]} can be considered as an effective solution. Its fluoride-rich surface has a natural low tension condition to avoid extra treatments, and its moderate stiffness well balances the competition between sufficient feature resolution and conformal contact capability in a relatively low pressure setting.

(2) NIL resist systems. Although thermoplastic materials are still vastly used in thermal NIL applications due to simple patterning mechanism by raising the temperature above their glass transition temperatures (T\textsubscript{g}). The associated extreme temperature and pressure requirements greatly limit the application scenarios to perfectly flat and robust substrates. The thermal expansion mismatch problem \textsuperscript{[82, 89]} between the mold and the substrate at elevated temperatures will significantly impact the pattern transfer fidelity.
Under such circumstances, UV NIL \cite{90-92} draws extensive attention since it provides room-temperature, low-pressure NIL operations on low-viscosity UV-curable resist systems, and a transparent flexible polymer mold will be a perfect match to it. Compared with thermal NIL resists, UV NIL resist is a more complex system containing various components to exhibit diverse and desired properties, such as high stiffness, great chemical stability, etching resistance and moderate surface tension upon curing. Each component must be carefully selected and evaluated to ensure ideal mold separation and pattern transfer. Two UV NIL resist systems both based on dense silica-like monomers but different polymerization mechanisms are investigated in this work to establish new recipes to greatly enhance the overall performances over those commercial products.

1.3 Dissertation structure

In this dissertation, a complete tool chain for nanopatterning with flexible NIL molds is introduced, including (1) various implementations to create large-area NIL master mold with novel complex nanostructures, all starting from imprinting of a basic grating arrays and manipulation of the transfer of Cr etching masks; (2) a fully polymer-based flexible NIL mold design from fluorinated material selection, high-throughput large-area duplication from masters, and its UV NIL applications in roller imprint and overlay-controlled alignment; (3) UV NIL resist systems both based on novel high-performance silsesquioxane monomers with tremendous advantages over current UV resist designs; (4) Transfer printing of metallic nanostructures using flexible NIL mold as the carrier for fast and high-throughput patterning onto traditional rigid substrates and many delicate unconventional substrates like thermal plastics and PDMS.
Specifically, chapter 2 reviews detailed designs and implementations of generating NIL mold with diverse features, including pillars (from 1 µm to 135 nm pitch), triangles (1 µm pitch) and moiré patterns. Chapter 3 discusses a fluorinated polymer based flexible hybrid mold architecture, namely high-fidelity flexible mold (HiF2M) and its capability to deliver room-temperature moderate-pressure UV NIL on PET substrate with a custom roller machine. Chapter 4 studies two UV resist systems with silica-like silsesquioxane monomers and other high-performance supporting components to deliver sub-30nm high-fidelity and stability patterned polymer structures for functional material transfer or for use as structural layer. Chapter 5 focuses on utilizing flexible mold to direct transfer pre-pattern metallic features onto target substrates with great integrity and large area. Finally, chapter 6 concludes the dissertation with the opportunities of future studies.
Chapter 2

Complex Nanostructure Fabrication

2.1 Introduction

High-quality master mold is the foundation of nanoimprint lithography, and there is a great challenge to effectively integrate high-resolution, high-throughout, low-cost and large-area characteristics in master mold fabrication with current nanopatterning techniques. For photolithography patterning, the lamp based photolithography tools are only able to deliver 300-nm minimum features \([93-94]\). Although excimer laser based systems with 193 nm ArF and liquid immersion upgrades scale down the feature sizes below 50 nm \([95-96]\), the access to these tools is fairly limited due to the facts of high cost and complexity \([97]\). Electron-beam lithography is capable of sub-20 nm feature resolution \([98-99]\) with custom patterns and maskless direct writing, but its low throughput presents a considerable obstacle to feasible large-area mold fabrication \([100]\). Several emerging patterning methods show potentials and more challenges: Directed self-assembly of block copolymers is advancing to sub-10 nm dense and ordered nanopattern formation \([101-102]\), but great efforts are still needed to identify and control defect sources for large-area capability \([46,103]\). Nanosphere lithography creates densely patterned arrays, but lacks long range order which often only results \(<100 \mu\text{m}\) uniform area size \([104-105]\).
To address this challenge, a series of NIL master mold fabrication approaches were developed, which utilized laser interference lithography (LIL) \[106-107\] to create large-area uniform gratings with different pitches and created more complex nanopattern array by combining NIL, multi-layer material stack and controlled etching mask deposition. LIL is a maskless photolithography to expose a photoresist layer with two or more coherent laser beams, and it has advantages in low cost, high throughput, no defect source due to substrate contact, large area and configurable pattern generation in terms of pitch and pattern geometry. 4-inch wafer scale photoresist gratings with 200-1000 nm pitches \[108\] were able to be formed in one-step LIL with two beams from 351 nm Ar laser source, and further transferred into SiO\(_2\) substrates.

The thermal oxidation SiO\(_2\) on Si substrate is selected as the master mold material because: (1) high-quality SiO\(_2\) can be grown from Si wafers in a low-cost, high-throughput, highly-controllable process; (2) grown SiO\(_2\) has ideal mechanical strength \[109\] and chemical stability to sustain in harsh conditions in terms of temperature, pressure and solvents; (3) SiO\(_2\) has a mature RIE recipe with CF\(_4\)/H\(_2\) combination \[110-113\] resulting in fast etching rate (56 nm/min), good etching selectivity (>3) to Si substrate etching for self-stopping etching technique, and steep sidewall profile (> 85\(^\circ\)); (4) natural silanol-rich surface is ideal for anti-adhesion treatment with silane reagents \[114-115\].

In this chapter, three processes will be introduced to build diverse nanopatterned NIL master mold by manipulating the etching mask shape in post-NIL steps so it can carry modified pattern information into the substrate by etching. The etching mask manipulations include (1) inversion with extra stacked sub-layers, and (2) union and/or multiplication with stacking mask layers.
2.2 Tri-layer process

It is obvious that the conventional pattern transfer method by depositing Cr directly to a substrate with patterned NIL resist layer will generate the Cr etching mask which has the same feature as the rising patterns of the master mold. This is intrinsically convenient for high-fidelity and fast mold duplication, but less flexible to create complex patterns from a certain mold. In this session, a tri-layer process was introduced to create inversed features from any master mold by manipulating the Cr pad transfer.

2.2.1 Tri-layer material and assembly

The tri-layer process starts from creating a stack of three consecutive thin layers of materials on top of the target substrates. First, an 80 nm-thick ARC layer (Antireflection coating XHRiC-16, Brewer Science, Inc.) is formed by spinning the ARC solution at 4000 rpm and baked at 180 ºC for 30 min. The fully cross-linked ARC is solely the Si-free thermoset polyimide, which is known for good chemical resistance in organic solvents, excellent mechanical properties and surface adhesion \[^{116-118}\]. Also the ARC layer can be either selectively patterned by O\_2 RIE at a typical rate of 35 nm/min \[^{110}\], or thoroughly stripped off with a standard 15 min RCA-1 cleaning (H\_2O\_2 : NH\_4OH : DI water = 1 : 1: 5 in volume, 90 ºC for 10 min ), and these properties provide the mature basis for the tri-layer process design. Above the ARC layer, there is a 15 nm-thick SiO\_2 layer by electron-beam evaporation, to serve as the etching mask to the beneath ARC layer and carry any transferred pattern from the top layer. On the top of the stack is a thermoplastic imprint resist (NXR-1025, Nanonex Corp.) ready for NIL patterning.
To use the tri-layer stack to transfer reversed master mold patterns, the original master patterns are first imprinted into the top-layer resist (Figure 2.1a) and transferred down to the mid-layer SiO₂ as Cr masks by RIE etching, E-beam evaporation and lift-off (Figure 2.1b). Two consecutive RIEs with CF₄/H₂ (33/7 sccm, 50 mTorr, 300 W) and O₂ (10 sccm, 1 mTorr, 50 W) respectively remove the SiO₂/ARC stack on the unmasked area and expose the target substrate (Figure 2.1d). A following Cr deposition generates the exactly reversed mask patterns to the original master patterns right on the target substrate (Figure 2.1e), and then the remaining tri-layer stack is removed by the standard RCA-1 cleaning (Figure 2.1f). Upon the substrate etching, the reversed Cr masks will transfer the patterns into the substrate material.
2.2.2 135 nm-pitch pillar mold fabrication by tri-layer process

Based on the tri-layer process, topologically complex nanostructures can be built with simple grating arrays. One example to illustrate the capability of the tri-layer process is the fabrication of a 135 nm-pitch pillar mold by using a grating master mold and the tri-layer approach on a 4-inch full-wafer substrate.

Figure 2.2 Schematics of a 135 nm-pitch pillar mold fabrication with the tri-layer process

Figure 2.2 shows the complete process flow of the fabrication of a 135 nm-pitch pillar mold:

(A) A 4-inch Si wafer with 130 nm-thick dry thermal oxide layer on top was used as the patterning substrate. 80 nm-thick ARC (ARC: PMA = 2: 1 in volume) was coated on the substrate by spinning at 2000 rpm for 60 s, and baked on a 180 ºC hotplate for 30
mins to reach the complete cross-linking. For a better ARC film formation, the oxide substrate was baked at 180 °C for 5 mins before the ARC coating to remove the surface moisture, and the ARC solution was filtered with 0.2 μm-diameter PTFE filter to eliminate unexpectedly cured polyimide clusters. After the bake, 15 nm-thick SiO$_2$ was deposited on top of the ARC layer by E-beam evaporation at 0.4 Å/s (Figure 2.2a).

(B) To create Cr etching masks, 110 nm-thick NXR-1025 thermal nanoimprint resist was coated on the substrate, and followed by a thermal NIL (200 Psi, 130 °C, 4 min) with a 135 nm-pitch grating master mold of 50 nm-width and 50 nm-height. The residual layer was etched away by an oxygen RIE (1 mTorr, 10 sccm, 50 W) for 100 s, and 10 nm-thick Cr was deposited on with an E-beam evaporation at 0.3 Å/s. A throughout lift-off in acetone left 70 nm-wide Cr grating lines on the substrate (Figure 2.2b).

![Figure 2.3 SEM images of (a) 10 nm-thick Cr mesh etching mask after two orthogonal Cr grating transfers, and (b) top view of the tri-layer assembly after SiO$_2$/ARC under-layer etchings](image)

Figure 2.3 SEM images of (a) 10 nm-thick Cr mesh etching mask after two orthogonal Cr grating transfers, and (b) top view of the tri-layer assembly after SiO$_2$/ARC under-layer etchings
(C) A second Cr grating lines transfer with the same parameters in step (b) from the orthogonal direction was performed to create a Cr mesh layer (Figure 2.3a) as the final etching mask. The average opening hole size was about 65 nm. It was confirmed that the top thin SiO$_2$ and ARC layers together showed a flat surface with great mechanical and chemical stability to carry the uniform and high-resolution Cr patterns in harsh processes like nanoimprint with high pressure and lift-off with acetone spray.

![Inversed square Cr pad arrays on the oxide substrate with 135 nm pitch and 65 nm width](image)

Figure 2.4 Inversed square Cr pad arrays on the oxide substrate with 135 nm pitch and 65 nm width

(D) Two brief RIE etchings exposed the oxide substrate: The first CF$_4$/H$_2$ RIE (50 mTorr, 33/7 sccm, 300 W, 20 s) removed the thin evaporated SiO$_2$ and the second oxygen
RIE (1 mTorr, 10 sccm, 50 W, 3 min) opened the pathway through the ARC layer (Figure 2.3b). The top Cr mesh mask protected the beneath material stack and maintained the pattern transfer fidelity with ideal etching resistance in both RIE processes. Again, a 7 nm Cr deposition transferred the etching mask further down to the oxide substrate, and one 5 min cleaning in RCA-1 at 90 °C lifted all upper layers away from the substrate, except for the Cr mask. After the processes above, a Cr mask layer of 135 nm-pitch 65 nm-wide square arrays were generated on the target oxide substrate, which were exactly the inversed patterns of the upper Cr mask (Figure 2.4). The tri-layer assembly conducted this designated pattern transformation with an ideal pattern transfer yield (> 99.5%).

(E) Finally, the 65 nm-wide SiO$_2$ square pillars with 130 nm heights were formed on the substrate by etching away the oxide layer (CF$_4$/H$_2$ RIE, 50 mTorr, 33/7 sccm, 300 W, 3 min). The remaining Cr mask was completed removed with the CR-7 Cr etchant. The substrate was then functionalized with hydrophobic silane MRA agent to serve as a NIL master mold (Figure 2.5).

Based on the same process design, square pillar molds with different pitches (e.g., 1 μm, and 400 nm) were fabricated using corresponding grating master molds, from which even more complex nanopattern arrays can be created when other unconventional techniques are incorporated.
2.3 Shadow evaporation

E-beam evaporation is a line-of-sight physical vapor deposition (PVD) technique \[^{119}\], so it offers structural and morphological control of the deposited films \[^{105, 120-121}\] by using pre-patterned substrates and manipulating the incident angle between the collimated evaporation beam with the substrate surface normal. In this session, we demonstrated a novel fabrication approach to generate 1 \(\mu\)m-pitch triangular pillar arrays by applying multiple shadow evaporations and a tri-layer stack.
2.3.1 Angle-controlled shadow evaporation

Multiple shadow evaporations are typically applied between the nanoimprint and resist residue etching, to not only cover the outer surface of the NIL patterned resist with a firm and thin Cr mask layer, but also leave the inner surface intact. So the RIE pattern transfer fidelity is defined by the Cr mask geometry, same as that of the initial imprinted resist, and won’t be deteriorated by resist lateral dimension change during RIE. At the same time, using a thicker initial resist layer is feasible since the Cr mask can create the post-RIE standalone resist structures with a higher aspect-ratio to greatly facilitate the lift-off process.

![Diagram of angle-controlled shadow evaporation](image)

**Figure 2.6 High-fidelity grating pattern transfer with NIL and shadow Cr mask**

The Figure 2.6 illustrates a NIL pattern transfer process from a grating master mold (50% duty cycle and 1:1 aspect ratio), and it adopts two symmetric shadow evaporations for high-fidelity transfer. Similarly, four consecutive shadow evaporations with 90°
rotation increment can be used in order to accurately transfer Cr mask patterns from imprinted resist with a pillar master mold. In the two examples above, 30% resist residual layer overetching is feasible to achieve large-area uniformity without inducing resist lateral geometry changes.

When the substrate is packed with more complex 2D pillar resist patterns, the characteristic line-of-sight and self-align shadow evaporations can enable the formation of novel 2D arrays, by first generating particular Cr masks on the inner surface of the patterned resist.

2.3.2 2D shadow evaporation mechanism

Figure 2.7 illustrates the shadow effect when the beam from the source material is reaching a rising resist pillar (square section, side s and height h).

![Figure 2.7 Shadow formation when a tilted source beam is used](image)
The resist pillar top surface is projected in the substrate with 1:1 scale as a shadow frontend stretched out from the pillar. Different from any previous 1D shadow evaporations on recessed resist patterns, a 2D spatial angle splits into two angle components which control the final shadow projection:

(1) $\alpha$ is the angle between the beam and its projection in the substrate plane, and it determines the stretching distance of the resist top surface projection as $h \cdot \cot(\alpha)$.

(2) $\beta$ is the angle between the beam in-plane projection and the side of the resist top surface, which controls the shadow stretching direction.

Using the shadow properties discussed, a process to form triangular patterns after two consecutive well-placed Cr shadow evaporations is designed (Figure 2.8):

![Diagram of shadow evaporation process](image)

**Figure 2.8** Design to form triangular patterns after two consecutive symmetry shadow evaporations

(1) Resist pillar array with square top-view profile (pitch $p$, height $h$ and side $s$) is first created by imprinting with a square hole master mold with desired inversed patterns on mold substrate (Figure 2.8a).
(2) The first shadow evaporation with controlling angle components $\alpha$ and $\beta$ covers a thin Cr mask layer on to the top resist surface, leaving a stretching shadow area without Cr blocking as future resist etching opening (Figure 2.8b).

(3) The other symmetric shadow evaporation mirrors a second shadow area behind the resist pillar. The overlapping area appears in both Cr deposition shadows is free of Cr masking effect, which has a shape of isosceles triangle with two $(90^\circ - \beta)$ angles (Figure 2.8c). When $\beta = 30^\circ$, an equilateral triangle shadow is formed.

In order to get the exact triangular patterns, several conditions should be met for each pillar:

(1) its 1$^{\text{st}}$ shadow area must not overlap the 2$^{\text{nd}}$ shadow area of its closest neighbor in the same row:

$$2h \cdot \cot(\alpha) \cdot \sin\beta < p + s$$

(2) its shadow stretching distance must be larger than the length of either isosceles side of the triangle:

$$2h \cdot \cot(\alpha) \cdot \sin\beta > s$$

Given a particular master mold and designated triangular area profile, the specific process can be designed by carefully selecting the angle component $\alpha$ and $\beta$. 
2.3.3 1 µm-pitch triangular pillar mold by shadow evaporation and tri-layer process

The procedure below describes the complete process flow to create a 1 µm-pitch triangular pillar mold by combining shadow evaporation and NIL by a 1 µm-pitch square hole mold:

(A) A 1 × 1 inch$^2$ Si substrate with 200 nm-thick dry thermal oxide layer on top is coated with 250 nm-thick NXR-1025 thermal nanoimprint resist and baked at 110 ºC for 5 min.

(B) A thermal NIL (250 Psi, 130 ºC, 4 min) with a 1 µm-pitch hole array master mold with 500 nm-width and 200 nm-depth square openings is performed (p = 1000 nm, s = 500 nm and h = 200 nm), and reversed resist square pillar arrays are formed with a 210 nm-thick residual layer. The shape of imprinted resist pillar plays the critical role in the incoming triangular opening definition, so 250 Psi (maximum working pressure for NX-2500 imprinter) is selected to better fill resist into recessed area in the master mold and get resist pillars with satisfactory side wall angle close to 90º.

(C) Two 5 nm-thick Cr shadow evaporations with $\beta = 30^\circ$ are performed to create an equilateral triangle area. Based on the previous restrictions previously discussed, $\alpha$ component must be chosen between $7.6^\circ$ and $21.0^\circ$. The mean value $\alpha = 14^\circ$ is actually selected to allow a large handling error in manual alignments of two shadow evaporations. Figure 2.9 shows the 1 µm-pitch triangle array formed after these two Cr shadow evaporation, in which all triangles present identical shapes.
Figure 2.9 Triangle array formation after two consecutive Cr shadow evaporations

(D) After the first two symmetric Cr shadow evaporations, both equal sides of an isosceles triangle are clearly defined by Cr boundaries, but the bottom side of the triangle still has resist exposed with inferior lateral protection, so large line roughness will be induced during the following long-time thick resist residual layer etching process. To solve the potential problem, an extra 5 nm-thick Cr evaporation with angle components $\alpha = 15^\circ$ and $\beta = 180^\circ$ is adopted to shield the exposed resist side wall associated with the triangle bottom side.

(E) An oxygen RIE (1 mTorr, 10 sccm, 50W, 10 min) etches through all unmasked triangular resist regions to reach the SiO$_2$ substrate.
Figure 2.10 Triangular Cr pads on the substrate: (a) defined by only two shadow evaporations, leaving the 3rd side of the triangle insufficiently protected which induced large line roughness during resist residue etching; (b) defined by use an extra shadow evaporation to cover the 3rd triangle side and smooth Cr boundary was acquired.

(F) E-beam evaporation deposits 10 nm-thick Cr etching mask onto the SiO2 substrate through the triangular holes, and a lift-off in acetone removes the resist layer and covered top Cr layer completely, leaving only 1 µm-pitch triangular Cr pad array on the substrate. Figure 2.10 compares the Cr pad transfer results with and without a 3rd protective shadow evaporation to shield the 3rd side of the triangle which is aligned with the resist pillar in-plane projection. The comparison clearly demonstrates its effectiveness with greatly reduced line roughness. A slight deformation of the original isosceles shapes of Cr triangles also indicates this extra shadow evaporation has a strict requirement on angle alignment accuracy to
not only protect the line feature but also maintain the designed triangle geometry in terms of each angle value.

(G) Finally, the corresponding SiO$_2$ triangular pillar array is formed on the substrate (Figure 2.11) by etching away the thermal oxide layer (CF$_4$/H$_2$ RIE, 50 mTorr, 33/7 sccm, 300 W, 4 min). The remaining Cr mask pads are striped with the CR-7 Cr etchant. The fabricated mold surface was then functionalized with hydrophobic silane MRA agent to serve.

![Figure 2.11 1 µm-pitch triangular pillar array master mold on SiO2 substrate](image)

2.4 Double Imprint

Compared with two previous methods, double imprint approach is fairly straightforward with the goal to populate the local nanopattern density. The first NIL was performed and a thin Cr etching mask layer is transferred to the substrate, and the second
round of NIL and Cr mask transfer is consecutively conducted right on the same substrate, so it will provide doubled Cr pattern quantity and local density and be shaped in the substrate material as a new master mold. The thin Cr mask layer generated in the first NIL and transfer presents little impact on the second Cr mask transfer, so the second NIL can maintain the same resist coating and NIL parameters without modification.

Figure 2.12 10 nm-thick Cr bowtie-shape mask patterns made by double imprinting of a 1 µm-pitch triangular pillar master mold

Figure 2.12 shows a bowtie array of Cr pads fabricated by adopting two consecutive NILs and Cr mask transfers of the same triangular pillar master mold. Not only the local triangle density is doubled, but also the closest triangles form a bowtie pair with greatly reduced tip distance (~200 nm) compared with the original triangle pitch of 1 µm, which is desired by many plasmonic device applications based on nanogap bowtie structures.
By etching into the underneath SiO$_2$ substrate, a bowtie pillar mold is generated which can be used to produce the same complex bowtie arrays in a simple, large-area and high-thought way.

Although double imprint is very simple to adopt for pattern multiplication, there is still a great challenge to maintain long-distance feature uniformity due to lack of an effective alignment approach to control the relative displacement between two groups of Cr masks. The alignment error due to mold rotation in the second NIL is the dominating factor to impact the long-distance order, especially for patterns with a smaller pitch and a denser arrangement. On the other hand, such inevitable rotation provides the foundation to create interesting moiré patterns with quick double imprint.

A moiré pattern is a superimposed pattern when two identical patterns are overlaid and displaced or rotated a small amount from each other $^{[122]}$. These patterns can be produced deliberately by graphic arts $^{[123]}$, photographic tools $^{[124]}$ and electronic displays $^{[125]}$, and the applications are currently extensively studied in high-resolution microscopy $^{[126]}$, image processing $^{[127]}$, navigation $^{[128]}$, strain measurement $^{[129]}$ and many other cases. Figure 2.13 shows the superposition of two identical periodic dot arrays with a placement angle difference. Because of the periodicity of the two layers, the overall pattern is also periodically repeated throughout the superposition, generating a periodic moiré pattern. Each ring-shape moiré pattern in the image shows an average size of 7 times of the original dot array pitch. Considering the dots are constructed with a certain type of dielectric material like SiO$_2$, the local dot density difference introduced in the moiré pattern creates a local refractive index difference. At the same time, the periodic moiré pattern formed a new array with the pitch much larger than the original dot array, into
micrometer scale. Therefore, such moiré pattern can naturally serve as a dielectric micro lens array in potential application, and the fabrication of the corresponding double pillar array master mold is worth investigating to enable the large-area production.

Figure 2.13 Moiré pattern created by two identical dot array (0.4:1 diameter/pitch ratio) with 25° relative rotation

The fabrication of a double pillar mold is straightforward: The first NIL and Cr mask transfer are performed on a 4-inch SiO₂ wafer. A Cr dot array of 200 nm pitch, 70 nm diameter and 10 nm thickness is formed after resist lift-off. The second NIL and Cr mask transfer is carried out next, and 30° angle rotation is applied in the orientation adjustment. Cr dot moiré pattern is now available on the substrate, and further etched into the SiO₂ substrate as the new master mold. Figure 2.14 shows the new double pillar mold with 1.4
µm-pitch moiré pattern. When the rotation adjustment increases from 0 to 45°, the moiré pattern period is decreasing. Due to the symmetric property of the original dot array, rotation in 45° - 90° has the same effect as its complement angle.

Figure 2.14 The SiO₂ double pillar master mold with 1.4 µm-pitch moiré pattern. The original pillar array has a pitch of 200nm and diameter of 70nm. The relative orientation rotation is about 30°.

Combining all discussed three nanopatterning approach, even more complex features can be built in a convenient way. Figure 2.15 presents the double hole master mold combining (1) pattern multiplication by double imprint, (2) tri-layer stack to inverse pillar features into holes, and (3) shadow Cr evaporations to protect hole pairs with sub-10nm spacing during resist residue etching process. Many other unique master molds have been
built based on these methods, and more are coming with careful designs and implantations.

Figure 2.15 The SiO$_2$ double hole master mold fabricated from the double pillar mold.

2.5 Summary

Diverse NIL master molds with complex nanopattern arrays were built from basic 1D grating molds, which were made by laser interference lithography with large-area, high-throughput, high-resolution and low-cost advantages. Manipulation of the Cr etching mask patterns is the key step to create new features, and it includes but is not limited to pattern inversion, multiplication and tailoring. To realize each specific operation, different approaches were introduced with feasible demonstrations: (1) 135 nm-pitch square pillar array was fabricated with a tri-layer material stack to inverse a mesh-shape
Cr mask pattern originally defined by imprinted top resist layer; (2) 1 μm-pitch triangular pillar array was formed by multiple Cr mask depositions with well controlled shadow angles, which tailored the overlapping Cr free region based on a straight resist pillar with square top-view profile; (3) Several new patterns by executing consecutive Cr mask transfers onto the substrates so that the pattern density was doubled and moiré features were able to be acquired by introducing a rotation angle to the substrate in the second NIL. Even more unique and useful features can be made by integrating these methods in the single fabrication design. These new master molds will generate novel nanophotonic devices in one-step large-area. High-throughput and low-cost NIL.
Chapter 3

PFPE-based Flexible Hybrid Mold for Nanoimprint

3.1 Introduction

The mechanical properties of the nanoimprint mold material play the dominant roles in pattern transfer capabilities. The common hard mold material typically shows 50-200 GPa Young’s modulus (Figure 3.1) \(^{[130]}\), which features less than 10 nm patterning resolutions \(^{[131]}\). However, the nanoimprint with hard molds normally requires more than 200 Psi working pressure to achieve the overall conformal contact on a 4-inch area, and demands an extremely flat mold surface for the uniform working pressure distribution. These hard mold materials also generally possess hydrophilic surface properties, so they need extra chemical hydrophobic surface treatments \(^{[132-134]}\) to facilitate the mold separations after imprinting. The short life span of the thin-layer hydrophobic coating greatly impacts the continuous operating capability of a hard mold \(^{[135-136]}\). The hard molds also rely on the large-area premier-quality substrates and complex fabrication processes to build master patterns on, which inevitably increase the unit cost in final massive production.
To address the weaknesses of hard mold materials in nanoimprint applications, polymer-based flexible molds were widely studied \cite{86, 87, 137, 138}. The Young’s modulus of a potential polymer candidate is located in 10 MPa – 1 GPa range, which promises the sub-50 nm patterning resolution and ideal contact by applying a moderate pressure. The truth that most polymers are fully cured via reactive groups from deliberately mixed pre-polymer solutions \cite{139} opens a feasible engineering path to further modify the physical and chemical properties by adding functional materials like surfactants and cross-linkers, and these modifications can effectively alter the polymer wetting property and stiffness to better fit the specific application needs. The liquid nature of pre-polymer solution also simplifies the mold fabrication and allows a fast replication by two-step spinning and curing. These raw pre-polymer materials normally show vast availabilities and low unit prices in the market, making polymer mold fabrication an affordable manufacturing approach. Besides all advantages above, ideal optical transparency properties of polymers make them used as natural UV nanoimprint mold materials.

**Figure 3.1 Young’s modulus of nanoimprint mold material**

![Diagram showing Young's modulus of various materials with labels for Young's Modulus, E, Large-area capability, and Feature Resolution.](image)
In this chapter, we proposed a complete PFPE polymer based flexible mold fabrication approach for UV nanoimprint and its applications in large-area high-performance novel plasmonic device fabrication with a roller machine. The demonstrated polymer mold features 90 MPa Young’s modulus to support sub-30 nm features, up to 50 cm by 20 cm large-area replication capability and intrinsic fluorinated functional groups for low surface tension without requiring hydrophobic post-treatment. Device fabrication in high-performance PlaCSH solar cells and D2PA biosensors with the custom pilot roller nanoimprint system were successful demonstrated.

3.2 PFPE Material

Compared to rigid mold, polymer-based mold is easier to fabricate, and generally has lower cost. To be considered as candidate for the nanoimprint mold, the material is expected to preserve the pattern fidelity at sub-50 nm scale for hundreds of patterning cycles. Meanwhile, the surface material should ensure a smooth mold release without generating defects, meaning that a low resist adhesion is required. In addition, the whole mold should remain flexible to be wrapped onto any setup.

Previously investigated polymer mold materials in flexible mold assembly include Polydimethylsiloxane (PDMS) (e.g., Sylgard 184) \cite{140}, Teflon \cite{141-142}, ethylene-tetrafluoroethylene (ETFE) \cite{86, 143}, etc. However, they all show some shortcomings that are not suitable for continuous imprint. For example, PDMS is incapable of patterning in sub-100 nm regime due to the low modulus and poor chemical stability; even the later developed hard PDMS (h-PDMS) with higher modulus of 9 MPa \cite{144-145} can only achieve the best resolution of 80 nm, still far from sub-50 nm resolution patterning. ETFE mold
requires surface bonding enhancement for resist (e.g., coating adhesion promoter) to reduce defect and avoid mold contamination. Once the mold is contaminated, it has to be replaced because thorough cleaning is difficult. Moreover, the polymer mold is expected to have sufficient air permeability so that the trapped air in nanoscale features can be released through the mold. Unfortunately, mold materials like ETFE or Teflon have poor air permeability, resulting in incomplete filling of features.

Perfluoropolyether (PFPE) is a promising fluorinated long-chain polymer to overcome those challenges. Its chemical formula is expressed as $F-(CF(CF_3)-CF_2-O)_n-CF_2CF_3$. With a moderate molecular weight from 3000 to 13000 g/mol, PFPE is in a liquid oil state, and it is already well known for its wide temperature range, general chemical and biological inertness and low surface tension \[1^{46}\]. As an efficient lubricant, PFPE oil covers many high-end application scenarios like clean room \[1^{47}\], vacuum environment \[1^{48}\] and spaceships \[1^{49}\]. To acquire a solid state PFPE polymer film with a much higher molecular weight to serve as the flexible mold material, the general approach is via the polymerization reactions of PFPE liquid monomers decorated with photo reactive (particularly to UV radiation \[1^{50}\]) functional groups, and the formation of an interpenetrating network.

Fully photocured PFPE has many advantages over previous materials, including: (1) high stiffness. The stiffness of mold material is critical for high-resolution patterning. PFPE features smaller monomer molecular weight (< 2000 g/mol) and shorter carbon chain, rendering higher bond density therefore higher stiffness \[1^{51}\]. (2) Low surface energy. Due to the fully fluorinated carbon chain, the surface energy is substantially lower (16-18 dynes/cm, compared to PDMS at 21.6 dynes/cm \[1^{52}\]). The fluorinated
polymer has less densely packed surfaces, leading to poorer van der Waals interactions with water. It is naturally hydrophobic, allowing smooth demolding without the necessity for mold pre-treatment. (3) Fast room-temperature fabrication. Unlike other mold materials, such as PDMS, for which the curing can take as long as 24 hours (or requires heating for shorter curing time), photocurable PFPE monomer can be UV cured within 120 seconds at room temperature, given a sufficient UV dosage. The fast curing essentially simplifies the mold fabrication and lowers the cost. (4) High chemical stability. Materials like PDMS suffer from chemical attack during the regular solvent cleaning. PDMS nanopatterns significantly deform in common solvents (e.g. acetone). In contrast, PFPE is highly chemically stable and resistant to most solvent clean process, allowing a longer lifetime for the flexible mold and easy cleaning options. Other advantages of PFPE include tunable polymer stiffness and UV transparency after curing. Table 3.1 compares the mold properties of PDMS and PFPE mold.

Table 3.1 Mold properties of PDMS and PFPE

<table>
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<th>PDMS</th>
<th>PFPE</th>
<th>PFPE Advantage</th>
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<tr>
<td><strong>Curing</strong></td>
<td>Heating</td>
<td>UV</td>
<td>Room temperature</td>
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<tr>
<td><strong>Curing Time</strong></td>
<td>3 hours</td>
<td>2 min</td>
<td>90x faster</td>
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<tr>
<td><strong>Surface energy</strong></td>
<td>21.6 dyn/cm</td>
<td>16 dyn/cm</td>
<td>No treatment required</td>
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<tr>
<td><strong>Solvent Compatibility</strong></td>
<td>Swelling in acetone</td>
<td>Stable</td>
<td>More stable</td>
</tr>
</tbody>
</table>

A photocurable PFPE pre-polymer solution can be prepared by thoroughly mixing a liquid PFPE monomer with (meth) acrylates functional group(s) and a free-radical type
photoinitiator, and a certain cross linker with high functionalities can also be added if a higher stiffness upon polymerization is required.

![Figure 3.2 PFPE-urethane methacrylate monomer formula]

In this work, a clear liquid PFPE-urethane methacrylate is selected (Fluorolink MD 700, ca. 1300 g/mol, Solvay) as the monomer, based on its structural advantages: (1) (Meth)acrylates are the most common free-radical UV curable monomers with low cost and high reaction rate; (2) PFPE-(meth)acrylates have the natures of low volumetric shrinkage upon polymerization and high polymerization level \(^{[150]}\); (3) Urethane polar structures but only enhance the miscibility with hydrogenated acrylates hence the compatibility with the common photoinitiator, but also offers a high mechanical strength in the cured PFPE network \(^{[153]}\). Figure 3.2 shows the formula of PFPE-urethane methacrylate monomer, and each R group stands for a UV reactive methacrylate functional group linked to the main PFPE liner chain backbone via a urethane group, so each monomer molecule features two functionalities.

There are adequate free-radical photoinitiators suitable for radical polymerization of the PFPE monomers, from which 2,2-Dimethoxy-2-phenylacetophenone (DMPA) is choose due to its well-studied overall performances \(^{[154]}\) including (1) a rapid and
efficient production of initiating radicals; (2) multiple-year stability with acrylate formulations; (3) The very short lifetime of the excited triplet state to avoid quenching.

A Small-molecule cross-linker agent trimethylolpropane triacrylate (TMPTA) with 3 branched reactive sites is blended into the pre-polymer solution, so that its copolymerization with PFPE monomer can produce a more complex interpenetrating network, compared with the linear chain architecture of PFPE monomer. The direct outcome is a boost in the polymer stiffness. However, the introduction of the cross-linker will also inevitably increase the polymer surface tension and impact the separation process \[^{155}\], so only small amount of no more than 0.25 % by weight can be added if necessary.

Therefore, a standard 100-gram pre-polymer solution can be made by mixing 96-gram PFPE monomer with 3.8-gram DMPA photoinitiator and 0.2-gram TMPTA cross-linker. The solution is then place in a 25-inch Hg vacuum chamber at room temperature for 30 s to de-gas, and sealed in a nitrogen bag for storage. The typical shelf time is no less than 180 days, if direct exposure to strong light sources is avoided.

3.3 High-fidelity flexible mold (HiF2M)

![Figure 3.3 Schematic of a HiF2M mold structure](image)
A novel flexible mold based on PFPE is developed, named “High-Fidelity Flexible Mold”, or HiF2M. This mold consists of three layers (Figure 3.3, from bottom to top): a thick flexible polyethylene terephthalate (PET) substrate, a bonding layer, and a high modulus PFPE layer carrying the nanopatterns on top. The 175 μm-thick PET substrate serves as a supportive structure to the whole mold, which is also sufficiently flexible to be wrapped onto curved surfaces. The PFPE layer has a high modulus of 90 MPa and hence ensures high fidelity patterning with sub-30 nm resolution.

3.3.1 Fabrication of HiF2M mold

The fabrication of HiF2M mold is shown in Figure 3.4. First, a thermal resist layer (NXR-1025, Nanonex) is spin-coated on a hard substrate and imprinted using the regular recipe. A negative-tone pattern is recorded in the resist (Figure 3.4a). Second, the PFPE
pre-polymer is spin-coated on the thermal resist at 1500 rpm for 1 minute. The sample is pre-cured under 40 mW/cm² UV light for two minutes in nitrogen environment (Figure 3.4b). The curing has to be conducted in a non-oxygen environment, as the oxygen intoxicates the photo-initiator in PFPE and precludes crosslink. Third, a UV-curable transparent adhesive (NOA 73, Norland Products, Inc.) is applied onto the cured PFPE surface, and then covered by the PET sheet. The entire structure is exposed to UV from the PET side in atmosphere for 5 minutes, until both the PFPE and adhesive layer are fully cured (Figure 3.4c). Manually peeling off the PFPE mold from the substrate completes the mold fabrication. Due to the low adhesion to the resist, the cross-linked PFPE delaminates at the interface between PFPE and thermal resist, with nanopatterns retained on the PEPE. (Figure 3.4d)

Figure 3.5 shows various HiF2M mold duplications from polymer masters (NXR-1025, Nanonex), and complementary pattern duplication is achieved by this approach. During the 200nm-pitch HiF2M pillar array duplication, a SEM inspection by sampling 30 areas (18×15 patterns/area) was performed to examine the duplication fidelity. Compare with the average pitch value of the polymer master (202.6 nm with 2.0 nm standard deviation), the duplicated HiF2M shows high fidelity from measured 201.0 nm average pitch with 2.4 nm standard deviation, which is only 0.8% in pitch deviation.
Figure 3.5 HiF2M mold duplications from polymer masters: (A) Polymer masters with patterned NXR-1025 thermal plastics nanostructures via a fast thermal NIL: 200nm-pitch hole array, gratings and pillar array; (B) Duplicated complimentary HiF2M patterns from polymer

Using the nanoimprinted polymer as a medium template to fabricate the HiF2M mold has several benefits: (1) PFPE molding is not directly on the master mold, but through this buffer template so that the master mold is protected from permanent damage during molding; (2) the mold patterns will be of positive-tone, same as the original master mold; (3) when multiple polymer templates are made from a single mold, parallel molding process is available, making the mold fabrication significantly faster.
3.3.2 HiF2M mold performance

![Image of nanopatterns on HiF2M flexible mold]

Figure 3.6 Nanopatterns on HiF2M flexible mold. (a) nano-pillar arrays with sub-30nm feature; (b) double-imprinted nano-pillar patterns, exhibiting a 5 nm-gap between pillars

The Young’s modulus of HiF2M mold is 90 MPa, measured by an atomic force microscope (AFM), which is much larger than the h-PDMS mold (~9MPa). Such high stiffness material allows high-resolution patterning. Figure 3.6a shows sub-30nm feature demonstrated in the HiF2M nanopillar mold. In another double-NIL nanopillar HiF2M mold showing Moiré pattern (Figure 3.6b), a 5 nm-gap between nanopillars can be identified, suggesting the capability of sub-10nm resolution duplication for the HiF2M mold.

Another feature of the HiF2M mold fabrication is the reusable polymer template (NXR-1025). It is critical to make sure that the nanopatterns on the template is intact after
each cure-and-transfer, so that the patterning is repeatable. Multiple transfers have been done by using the same polymer template. By comparing the patterns on the HiF2M mold between the first duplication (Figure 3.7a) and the 30th duplication (Figure 3.7b), it can be seen that there is no significant difference, suggesting that the polymer template is reusable without distortion, which is suitable for the multiple cure-and-transfer process.

![fabricated HiF2M mold](image)

**Figure 3.7 Fabricated HiF2M mold by using the same polymer template. (a) the 1st HiF2M mold; (b) the 30th HiF2M mold.**

### 3.3.3 Scaling up for larger-area mold

As described above, a flexible mold is normally duplicated from a pre-patterned hard mold and wrapped onto the designated working surface such as the main roller of a roller NIL machine setup. Due to the difficulty in large-area direct patterning, typically the original master mold is smaller than the target mold dimensions. Hence it is desired to develop a scaling-up method to fabricate larger-area flexible mold. A cure-and-transfer process is developed here (Figure 3.8). The fabrication is similar to the HiF2M mold
described in the previous section. After fully curing of PFPE (step 1), the UV-curable adhesive (NOA 73), which serves as the bonding medium, is coated and cured to bond PFPE onto PET (step 2). The polymer template is then peeled off (demolding) from PET and the PFPE pattern remains on the PET substrate (step 3). This process can be performed in a step-and-repeat manner on the PET for multiple times until the large mold is fully patterned. Since the demolding does not affect the polymer template, it can be reused immediately for the next cure-and-transfer process without any treatment or cleaning. Multiple polymer templates can be used to carry out the cure-and-transfer process in parallel, which is even faster.

Figure 3.8 Multiple cure-and-transfer for large area HiF2M mold fabrication

One may notice that there are two curing steps (1st curing for the PFPE, and 2nd curing for the adhesion layer). This design avoids the mix up of PFPE precursor and the
adhesive material. Another advantage is that only the PFPE-coated NXR-1025 is required to be located in a non-oxygen environment during curing. Previous study puts the entire structure (including PET substrate) into the chamber for curing, which is inconvenient and limits the mold area to the chamber capacity.

Figure 3.9 shows an example of a 500 mm×200 mm large flexible mold assembly featuring 400 nm-pitch nanomesh structures. It is fabricated by 8-time cure-and-transfer duplication from a single 4-inch template. Each cycle takes 7-8 min; thus it only requires an hour to make this roller mold. Compared to the several-hour budget for each transfer for the PDMS mold, this PFPE HiF2M mold has a significant advantage in fabrication efficiency.

Figure 3.9 Large HiF2M mold based on PET with 8-time cure-and-transfers
3.4 Imprint with HiF2M

3.4.1 Aligned UV NIL with HiF2M

The transparent nature of HiF2M provides a great potential to perform an alignment operation with the substrates when both alignment marks are available on HiF2M and the substrate. This will meet the requirements from the devices which demand high precision alignment to the crystallographic orientation of the substrate such as the side emitting lasers on InP.\textsuperscript{[156-157]}

Similar to the alignment setup in a photolithography mask aligner, the custom HiF2M aligner module consists of three components (Figure 3.10): (1) a top chunk with 3 × 1.5 inch\textsuperscript{2} transparent quartz observation window. A controlled vacuum channel firmly secures a HiF2M facing down to the sample substrate. The 125 µm-thick high-stiffness PET supporting backplane of HiF2M ensures that no mold deformation is induced by
such vacuum locking mechanism. The HiF2M contains device pattern information and a set of alignment marks. (2) a sample substrate holder plate is located on the bottom chunk, with 3-axis movement capability for alignment adjustments. The substrate is a 2-inch InP wafer pre-etched with a corresponding mark set and coated with a NIL resist layer. (3) two-eye microscopes feed the signal to CCD modules for monitoring the operation. The substrate wafer is first lifted to HiF2M with a close distance of 1 mm, so that the microscopes can spot the mark patterns on HiF2M and the substrate by adjusting the focus. Different from the photolithography mask, a HiF2M is a fully transparent “mask” and the mark shape is defined by the vertical edge of its boundary. Therefore, in order to clearly visualize the mark in HiF2M, mark pattern depth should be no less 100 nm to guarantee enough contrast of the mark edges. The HiF2M mold used in the following alignment practice has a 150 nm pattern height. On the other hand, the marks in the InP substrate should only possess a moderate vertical edge no more than 150 nm. The regular NIL resist coating has the thickness in 100-200 nm range, and steep patterns in the substrate will greatly impact the local resist film formation by blocking or absorbing the resist flow and produce reduced visual effect to clearly spot the mark boundaries.

While the 3-axis stage is adjusted for fine alignment modification, the substrate wafer is gradually lifted until the best alignment practice is achieved. The HiF2M and the substrate is then contacted into an entire assembly due to resist layer adhesion, and the assembly is transferred into the imprinter for pattern curing, transfer and separation. In practice, a Nanonex NX-2500 NIL machine (Figure 3.11) is adopted to carry out the discussed alignment operation with its integrated alignment module. Once the alignment is completed, the 2-inch substrate wafer is pushed to stick with the HiF2M surface
securely. Then the mold chunk is removed from the alignment module, and moved above the loading drawer of the imprinting chamber. The vacuum locking is switched to release the assembly into the chamber where NIL is performed.

![Image of Nanonex NX-2500 with integrated alignment module]

**Figure 3.11 Nanonex NX-2500 with integrated alignment module**

Figure 3.12 is the layout profile of the two alignment mark sets on HiF2M and InP substrate, respectively. Each set contains four marks at locations within a 2-inch wafer area, and two marks in the same row will be used for alignment operations for both mark sets. The two marks have the horizontal distance of 36 mm. The fine ruler-shape in-plane pattern is used to calculate the displacement error of each individual mark, so the orientation error can be calculated accordingly. Each finger pattern in the ruler structure has the same width of 3 µm and spacing of 5 µm.
Figure 3.12 Alignment mark sets on HiF2M and the InP substrate: (a) The full set of 4 mark groups; (b) zoom-in details of a single mark group (darker color and white color subsets are corresponding to the marks on HiF2M and InP substrate, respectively).

The alignment result as the pattern in imprinted resist layer is shown in Figure 3.13 for marks at the coordinates (-17.82, 10.18) and (18.18, 10.18) (unit: mm). The relative displacement error of either mark is counted and measured as (-6, 2) and (1, 9) (unit: µm). Considering the 3.6 mm horizontal distance of two marks, the orientation error is calculated as 0.11°, which shows a great alignment accuracy. In the total 5 alignment practices, the average absolute displacement is 8.1 µm, the average orientation error is 0.12°.
Figure 3.13 Alignment result showed as the relative displacement of the two mark layers: (a) and (b) are the mark region at the coordinates (-17.82, 10.18) and (18.18, 10.18) (unit: mm).

Figure 3.14 presents an imprinted 2-inch InP wafer after a fine orientation alignment. Not only the alignment has been demonstrated with only 0.11° rotation error, but also the images show great resist film integrity and uniformity on the fragile InP substrate, which means ideal resist adhesion to InP, clean separation with HiF2M, and safe pressure parameter to apply on InP wafers. The zoom-in SEM image also confirms the high-fidelity and high-resolution imprinting that HiF2M provides. 200 nm-pitch resist gratings with 150 nm height are successfully generated on InP substrate with well-tuned orientation. The future process will focus on building the side emitting devices in the patterned areas.
Figure 3.14 Imprinted resist pattern on InP substrate with orientation alignment: (a) image of imprinted 2-inch InP wafer. Each of the five patterning area consists of 200 nm-pitch gratings. (b) zoom-in SEM image of the resist grating patterns.

This alignment approach based on transparent HiF2M has no limitation on wafer size handling capability, as long as the alignment module can hold the substrate. So combined with the large-area HiF2M, fine alignment on larger wafers can be performed with little modification on the original process.

3.4.2 UV roller NIL with HiF2M

For batch nanoimprinting process, the long cycle time for each batch hinders it from high-throughput manufacture. Roller nanoimprint lithography\textsuperscript{[75-76, 143, 158]} was proposed to solve this problem, which features a continuous imprinting process. Similar to conventional imprint based on flat hard mold, the major steps include (a) resist coating, (b) mold contact, (c) imprint resist curing, and (d) mold-substrate release. Due to the difficulty of local temperature control and the long heating/cooling time\textsuperscript{[159]}, thermal
imprint \cite{160-161} is not preferred for roller imprint. Instead, UV imprint is more widely applied \cite{162-163}. The state-of-the-art throughput of roller imprint can be as high as 30 m per minute.

There are several advantages of roller imprint technique. (1) The continuous patterning approach dramatically increases the patterning area (theoretically limitless), which allows a high throughput. (2) The contact area of mold and substrate is much smaller, which requires less pressure to be applied. Meanwhile, the high resolution featured by nanoimprint is retained. (3) Demolding is performed in a “peel-off” style. Peeling the substrate off the mold requires much less force and reduces the defects, compared to the conventional direct separation for hard mold and substrate.

![Roller imprinter setup](image)

**Figure 3.15 Roller imprinter setup: (a) cross-section schematics (b) top view of three major rollers**

The Roller NIL machine designed and used in this work (Figure 3.15) comprises (1) one 6 inch-diameter 6-inch long polished steel active roller mounted by a large-area high-fidelity flexible mold (HiF2M), driven the external motor; (2) two 2 inch-diameter
rubber-covered passive rollers as the gap control roller and the separation roller, respectively. (3) the adjustable spring mechanism that insets a pressing force between the gap control roller and the roller mold as the imprint pressure; (4) a UV lamp for curing, permitting fast curing for UV-curable resins. 125µm-thick optical-grade PET thin films are selected as the sample substrate due to its ideal surface roughness, flexibility and chemical stability. NXR-2030 UV resist (Nanonex) as patterning material permits sub-5nm resolution, low viscosity and low curing dosage by itself. Upon applications, different primer layers can be applied between NXR-2030 and PET for better lift-off or bonding performance.

**Figure 3.16 Patterned NXR-2030 via UV roller NIL with sub-30nm resolution and conformal contact:** (A) Imprinted 130nm-pitch NXR-2030 hole arrays with 30nm-diameter; (B) Conformal imprinted 200nm-pitch pillar arrays completely covering a dust defect with 500nm diameter.

Using HiF2M molds and the roller nanoimprinter machine, UV roller NIL was performed: 125µm-thick optical-grade PET films were tailored into 4-inch wide strips first. An 8nm-thick adhesion promoter layer was dispersed and the PET substrate was
briefly baked in 135°C for 1 min. Then a 100nm-thick 5% NXR-2030 UV resist layer was dispensed on PET substrate and sent through the roller module for pressing and cured using the UV lamp with 40 mW/cm² power density for 30s. Due to the flexible nature of HiF2M molds and the low viscosity of NXR-2030 resist, 15 Psi working pressure is sufficient for pattern transfers, which is low compared to the value when using a rigid mold so that it required no complex mechanism for generating the working pressure. To suppress the oxygen inhibition issue from UV resist curing, then nanoimprinter setup is immersed in nitrogen environment. The patterning throughput is around 8 inch × 4 inch per minute. Figure 3.16 shows the demonstration of sub-30 resolution UV roller NIL, and an ideal conformal-contact capability. Even in the presence of surface defect with several hundred nanometer size, the designated NXR-2030 patterns can still fully cover the sample area without vacancy, which is a key feature for maintaining the pattern transfer quality during the continuous roller imprinting process.

To exhibit the overall pattern transfer quality of HiF2M-based UV roller NIL, a HiF2M mold is first duplicated from a master mold with 400nm-pitch mesh structure (Figure 3.17a-c). The patterns on the HiF2M mold (Figure 3.17c) are found to be a high-fidelity replication of the master mold. The ridge width is 42 nm, and the square shape of the nano-patterns is well preserved, indicating sufficient stiffness of PFPE as a mold material. Figure 3.17d shows the demonstration of UV imprint by using this HiF2M roller mold. By comparing Figure 3.17d to Figure 3.17b, it can be demonstrated that the duplicated flexible roller mold renders the same performance in nanoimprint as the original master mold.
Feature fidelity is also of interest. In general, it is desired to have the patterns on the duplicated flexible mold exactly the same as the original mold. The ridge linewidth across the whole HiF2M mold is statistically analyzed and summarized in Table 3.2. It can be seen that after mold duplication, the average linewidth has only 0.7% difference to the master mold. The feature deviation $\sigma$ is unchanged. These facts indicate that the molding process for the HiF2M mold duplicates nanopatterns with high fidelity. The
duplicated mold perfectly preserves both pattern feature and pattern arrangement, and is capable to withstand external applied pressure.

Table 3.2 Feature size comparison between master mold and HiF2M

<table>
<thead>
<tr>
<th>Linewidth (nm)</th>
<th>Master mold</th>
<th>HiF2M</th>
<th>change</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.67</td>
<td>41.96</td>
<td>0.7%</td>
<td></td>
</tr>
</tbody>
</table>

| σ (nm) | 1.84 | 1.87 | 1.6% |

The high-fidelity duplication is verified by the study on the duplicated nanopatterns, where pattern pitch and feature size are analyzed to determine if distortion or deformation occurs during the molding process and imprinting process. Soft mold materials are easily distorted under external pressure. For periodic nanopatterns, pattern distortion induces significant change in the average pitch, or significant increase in the pitch deviation σ. Figure 3.18 is a summary of the pitch analysis for nanopatterns throughout the roller mold fabrication and roller NIL process. It can be found that from the master mold to the HiF2M mold, the average pitch has only 0.8% change, and the pitch deviation σ has no significant change (8.45nm for master mold, 9.03nm for HiF2M). SEM analysis has a 5 nm measurement error, and the measured change in both the average pitch and the pitch deviation σ are below this allowance value, meaning that no distortion is involved during the molding process. Similar high-fidelity UV roller NIL results are also proved by comparing the pitch difference between HiF2M mold and imprinted UV resist patterns, and only a slight change of 0.18% is observed.
A high-fidelity flexible mold for roller imprint is developed, featuring high-stiffness fluorinated polymer. The pilot mold achieves high-resolution patterning of 5 nm nanogaps with high fidelity. Large-area HiF2M mold is demonstrated by multiple cure-and-transfer process. The fabrication of HiF2M mold is demonstrated to be fast and low-cost, as a single cure-and-transfer can be completed within 8 minutes, a significant improvement to the several hours’ budget by using PDMS. The roller mold design and fabrication presented here is promising for large-scale roller mold manufacture.
Chapter 4

Silsesquioxane UV Nanoimprint Resist System

4.1 Introduction

Compared to conventional thermal nanoimprint lithography which typically requires 100+ °C high temperature and 200+ Psi high pressure, UV curing NIL \[^{164}\] has unmatched advantages such as (1) room-temperature operation with lower energy consumption, (2) improved batch fabrication speed by higher curing speed of UV curable resist, (3) better pattern fidelity and lower defect density due to the absence of extreme temperature and pressure induced pattern deformation, (4) relatively low operating pressure because of less viscous resists, therefore suitable to special rigid substrates with fragile mechanical strength, like InP wafers \[^{165}\]. Therefore, UV NIL is widely adopted by various nanoimprinting applications in a very fast pace, and researches on key UV NIL components are actively conducted across the globe \[^{164}\]. The success on previous PFPE-based HiF2M mold development provided us a leading position in UV NIL research since large-area, low-cost and UV transparent HiF2M is a naturally superior choice as high-performance UV NIL mold. Further effort is focus on developing advanced patterning materials, which are also known as UV curable NIL resists.
UV curable NIL resist is the material foundation to conduct UV NIL process. A well-developed UV-NIL resist system [166-167] must present several essential characteristics: (1) high UV curing speed, (2) Ideal chemical and physical etching resistance [168], (3) low volumetric shrinkage during polymerization [169], (4) low surface tension [170], (5) uniform film formation after spin-coating [171], and (6) low evaporation rate [172].

In this chapter, two types of Si-containing UV NIL resists based on Polyhedral oligomeric silsesquioxane (POSS) are developed with different photopolymerization mechanisms, and they exhibit unique advantages in particular application scenarios. They all share the same distinguished performances like strong etching selectivity as the mask, moderate volumetric shrinkage and sub-50 nm patterning resolutions, and they are completely compatible to existing HiF2M molds.

### 4.2 Polyhedral oligomeric silsesquioxane (POSS)

Silsesquioxanes (SSQ) [173-175] refer to a particular type of silicon compounds in which each silicon is linked to three neighboring oxygen atoms. SSQ has the general formula of \((R\text{SiO}_{3/2})_2\alpha\), and \(R\) can be an organic functional group from a wide variety of choices such as \(H\), alkyl, aryl, epoxide, halogen and many others. Although SSQs all share the same formula, their dimensional architectures can greatly vary from totally random structures to well-built ladder and cage structures. These variants have been successfully adopted in application cases such as (1) spin-on-glass low-k dielectric insulator [176], (2) functionalized OLED materials [177], (3) antimicrobial materials [178], (4) direct write negative tone electron-beam resist [179].
The term polyhedral oligomeric silsesquioxane (POSS) \cite{180-182} is the vivid description of cage-shape SSQ architectures with a silicon atom at each vertex. Although all POSS molecular forms with 6, 8, 10 and 12 Si vertices can be synthetized, the 8-vertex cages (RSiO\(_{3/2}\))\(_8\) (Figure 4.1) have been widely studied and commercialized in industrial production scale. POSS shows itself as a 1-3 nm diameter silica nanoparticle, which is a central silica cage core with an organic functional group tetrahedrally connected to each corner silicon atom. Such a hybrid structure perfectly combines excellent intrinsic mechanical properties from the inner core with adjustable polarity and chemical reactivity from the outer layer. The silica core presents high stiffness, high thermal and mechanical resistances, high plasma etching resistance, and high chemical stability. The outer layer of organic groups provides better solubility to common polymers by adjusting molecule polarity with specific functional group combinations. Therefore, POSS

\hspace{0.5cm} Figure 4.1 8-vertex cage POSS molecule
molecules can be utilized to enhance target polymer mechanical properties by physically blending them into the polymer matrix.

Furthermore, the flexibility on outer organic group selection promises a better approach to incorporate POSS molecules into polymers, which is via chemical copolymerization to form firm covalent bonding, and different polymerization mechanisms can be adopted upon application requests by using POSS with corresponding reactive groups. These characteristics attract great attention to POSS applications as NIL resist materials, especially UV NIL monomers, which has been considered as a promising field of advanced NIL technology.

4.3 POSS UV-NIL resist system

Generally speaking, a UV NIL resist system consists of the following components: (1) monomer \[^{166}\], (2) photoinitiator \[^{183}\], (3) diluent \[^{184}\] and (4) surfactant \[^{185}\]. POSS shows a satisfactory performance criterion to be a promising monomer building block, it still relies on the selection of those functional components to maximize the overall performances of the resist system. In this session, the major principals of component evaluation and selection is discussed.

4.3.1 POSS monomer

Monomers in a UV-NIL resist system are the basic reactive building blocks of the polymer network when the polymerization reaction of monomers changes the liquid resist to solid with the absorption of UV radiation. POSS-based monomer is one of the best
choices, because the cured polymer generally inherits the mechanical characteristics from parent monomers and POSS molecules have plenty superior properties in term of stiffness and stability. POSS monomers are classified according to the UV polymerization mechanisms into several types, among which the mainstream focuses are (1) free-radical polymerization type \[186-188\], and (2) cationic ring-opening polymerization type \[189-191\]. Either type requests unique POSS outer organic groups and exhibits its specific curing properties with advantages and drawbacks, so proper POSS monomers should be carefully investigated and selected to meet designated application scenarios.

4.3.1.1 Free-radical polymerization POSS monomer

Free-radical polymerization is the most common type of addition polymerization, where individual monomers are consecutively added to an active site on the growing polymer chain or network \[192\]. A free radical is a molecule with an unpaired electron, and it is highly reactive with strong tendency to form a stable electron pair by breaking bonds on another molecule. A certain type of photoinitiator is required to convert a monomer into a radical first. The photoinitiator can break into radicals upon absorption of photo energy and each of them links to and convert a monomer into a radical. Again, the exposed radical site reacts with another monomer so that such process continues to grow and propagating the chain into high molecular weight polymer until the termination process happens. There are three major advantages for free-radical polymerization: (1) Fast reaction rate \[193\]; (2) High molecular weight is obtained at low monomer conversion \[194\]; (3) Free-radical polymerizations have no by-products, unlike condensation type polymerizations.
Typical free-radical polymerization monomer contains at least one vinyl or (meth)acryl groups \[184, 196-198\] with carbon double bonds to enable radical polymerization. Regarding the available reactive POSS monomers with matched functional groups, a methacryl POSS \[195\] with 8 methacrylate groups (Figure 4.2) was selected. It has a colorless and odorless oil form at room temperature with 18-Poise viscosity (25 °C) and refractive index of 1.46 closed to native fused silica (1.45). Its multifunctional configuration occupies all 8 functional sites branched into different spatial directions so a complicated 3D polymer network can be formed with robust mechanical and chemical stabilities.

4.3.1.2 Cationic ring-opening polymerization POSS monomer

The ring-opening polymerization has been used in commercial UV curable polymer system such as epoxy resin \[199-200\] for a long time. The polymerization reactivity of a cyclic monomer is determined by both thermodynamics and kinetic factors. The thermodynamic factor refers to the stabilities of the cyclic monomer, which is dependent
on the strain in the ring structure: a higher strain results in less stable ring structure and higher reactivity of polymerization \(^{[201]}\). Among all variants, the highest strains are present in 3- and 4-membered rings. On the other hand, kinetic factor demands the presence of heteroatom in the ring (e.g., oxygen, sulfur, nitrogen, phosphorus and silicon) \(^{[202]}\) to offer a site for nucleophilic attack by photoinitiators, which starts the polymerization initiation and propagation phases by opening the ring. With both factors considered, POSS with decorated epoxide substituents (cyclic ether with a 3-membered ring) \(^{[203]}\) (Figure 4.3) is selected as the cationic ring-opening monomer for maximized potential reactivity. It has the similar density and solubility properties as the free-radical POSS monomer, with increased refractive index and viscosity.

![Figure 4.3 Glycidyl POSS monomer \(^{[203]}\)](image)

Table 4.1 lists the general properties of chosen free-radical and cationic POSS monomers. They have the similar molecular weights, densities and refractive indexes due to the presence of a common fused-silica cage core with close to 50% weight ratio of the
entire molecule. By blending extra additives, more designated characteristics can be introduced.

### Table 4.1 Typical properties of free-radical and cationic POSS monomer

<table>
<thead>
<tr>
<th></th>
<th>Methacryl POSS</th>
<th>Glycidyl POSS</th>
</tr>
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<tbody>
<tr>
<td><strong>Formula</strong></td>
<td></td>
<td></td>
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</tbody>
</table>
(C$_7$H$_{11}$O$_2$)$_8$(SiO$_{3/2}$)$_8$ | 
(C$_6$H$_{11}$O$_2$)$_8$(SiO$_{3/2}$)$_8$ |
| **Molecular Weight** | 1433           | 1388         |
| **Appearance**       | clear, colorless oil | clear, pale yellow, viscous liquid |
| **Density**          | 1.20 g/ml      | 1.25 g/ml    |
| **Refractive Index** | 1.46           | 1.51         |
| **Viscosity (25°C)** | 18 Poise       | 48 Poise     |
| **Solvent Solubility** | THF, acetone, ethanol chloroform, acetonitrile | THF, toluene chloroform |
| **Resin Solubility** | aromatic and aliphatic acrylic, epoxy, urethane, olefin resins | aromatic and aliphatic epoxy, urethane, acrylic, olefin resins |

### 4.3.2 Photoinitiator

A photoinitiator [204] is the chemical reagent that commences a photoreaction upon absorption of light and generates highly reactive species, and those species initiate chemical chain reactions of resist monomers with designated functional groups to form a solid homopolymers or copolymer network. A proper photoinitiator is chosen based on the polymerization mechanism of POSS monomer, which is associated with the types of functional groups: (1) free-radical photoinitiators for (meth)acrylate-based POSS resist and (2) cationic photoinitiators for epoxide-based POSS resist.
4.3.2.1 Free-radical photoinitiator

Figure 4.4 2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl)-1-butanone (BDMB) photoinitiator

Free-radical photoinitiators and polymerization approaches are widely adopted due to highest photoreaction rates by absorbing 300-400 nm UV radiation. Among all known free-radical photoinitiators, 2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl)-1-butanone (BDMB) (Figure 4.4) is the best choice [205-207]. Besides the efficient i-line (365 nm) absorption, BDMB has the following unique characteristics: (1) Extended absorption above 400 nm. Its 2-ethyl-2-benzyl substitution effectively stretches the absorption pattern into the visible range beyond 400 nm, which explains its higher curing speed in a metal-halide lamp light source. (2) Strong resistance of oxygen inhibition. The biggest drawback of free-radical photoinitiators is that they are vulnerable to oxygen in excited states [208-209], and incomplete polymerization of monomers is inevitable if excessive oxygen consumes too much photoinitiators. However, for BDMB, its tertiary amine radicals actively eliminate the peroxy radicals, which are mainly from the diffused
oxygen in coated resist, and such effect ensures a high polymerization degree. This permits a longer resist handling time before UV NIL without the need of complex nitrogen blanketing setup to purge oxygen.

4.3.2.2 Cationic photoinitiator

On the other hand, cationic photoinitiators and corresponding curing processes exhibit a major advantage over free-radical photoinitiators: cationic polymerization is not inhibited by oxygen due to a totally different initiation mechanism. This is a huge leap to eventually realize low-cost continuous UV NIL fabrication in the atmosphere since no expensive and bulky nitrogen blanketing subsystem is required anymore. Unlike free-radical polymerizations, initiation in cationic polymerization adopts a photoinitiator that is fully restored at the end of the polymerization and is not incorporated into the polymerization chain or network. There are mainly three types of cationic photoinitiators: aryl diazonium salts, onium salts and organometallic complexes [210]. The most commonly used photoinitiators for cationic polymerizations are onium salts, particularly triarylsulfonium salts with the general structures Ar3-S+·MtXn⁻ (MtXn⁻ represents a nucleophilic counter ion, and Ar means an aromatic functional group) [211-212], and they have high efficiencies for the ring-opening polymerization of epoxides in the short UV wavelength region (230 – 300 nm). The polymerization rates by triarylsulfonium salts are influenced by the size of the anions. Large anions exhibit faster curing, in the following order [213]:

\[
\text{SbF}_6^- > \text{PF}_6^- > \text{AsF}_6^- > \text{BF}_6^-
\]
Based on all the factors above, triarylsulfonium hexafluoroantimonate salt (654027, Sigma-Aldrich) (Figure 4.5) is selected as the photoinitiator to maximize the potential curing rate.

Besides the photoinitiator, isopropyl thioxanthone (ITX) is introduced into the system as an efficient photosensitizer to boost the UV absorption efficiency in short UV wavelength region with the absorption peak at 260 nm.

![Triarylsulfonium hexafluoroantimonate salts and 2-Isopropylthioxanthone](image)

**Figure 4.5 Cationic photoinitiator (triarylsulfonium salt) and photosensitizer (2-isopropylthioxanthone)**

### 4.3.3 Reactive diluent

Although POSS monomers themselves can be polymerized into homopolymers, the viscous nature of these POSS monomers prohibit the formation of sub-100 nm thick POSS dispersion by normal spin-coating method. Therefore, a certain solvent with a low viscosity is required, which serves as an effective diluent at least. Besides, since the resist solution will be photocured as a mixed reagent, the diluent component has to be equipped with the compatible reactive functional groups to the POSS monomers, which will create
a solid co-polymer network upon polymerization. So the reactive diluent will not only adjust the film thickness range, but also shift the mechanical strength and chemical resistance.

Another required characteristic is low evaporation rate, which indicates a weak tendency of diluent molecules to escape from the liquid form of the resist solution into an airborne vapor at room temperature. Low evaporation rate ensures a limited diluent loss during the resist coating and handling phases prior to UV NIL \[^{215}\], so it minimizes the impact to the resist film integrity and thickness uniformity from the process time variation. Secondly, low evaporation rate stretches the resist shelf lifespan by reducing the component loss during storage.

**Table 4.2 Typical methacrylate reactive diluent properties**

<table>
<thead>
<tr>
<th></th>
<th>Molecular Weight ( g/mol )</th>
<th>Vapor Pressure (mm Hg at 25 °C)</th>
<th>Boiling Point ( ºC )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Isobutyl methacrylate</strong></td>
<td>142.2</td>
<td>3.5</td>
<td>155</td>
</tr>
<tr>
<td><strong>Isobornyl methacrylate</strong></td>
<td>222.32</td>
<td>0.11</td>
<td>127 - 129</td>
</tr>
<tr>
<td><strong>Benzyl methacrylate</strong></td>
<td>176.21</td>
<td>0.034</td>
<td>95 - 98</td>
</tr>
</tbody>
</table>

To work with free-radical POSS monomers, 3 low-viscosity reactive diluents with monofunctional methacrylate groups were selected.

Table 4.2 shows the important properties related to the evaporation rates. Stronger intermolecular forces dominated by Van Der Waals forces are commonly responsible for
higher boiling points, lower vapor pressures and lower evaporation rates. The forces are normally enhanced by larger molecule surface area and molecular weight: Isobornyl methacrylate has the lowest vapor pressure mainly due to its molecular weight advantage; The linear chain structure of Isobutyl methacrylate has a larger surface area, compared with the compact ring structures presented in the other diluents, and it shows the highest boiling point despite of its smaller molecular weight. To find a proper diluent component, the rule of thumb is starting from the one with the lowest vapor pressure first. Besides, other factors must be taken into consideration to select the best candidate, such as the adhesion to regular substrate materials, good film quality and chemical safety.

In this work, Isobornyl methacrylate is used as the diluent for free-radical POSS system and neopentyl glycol di-glycidyl ether is chosen for ring-opening POSS system, due to their reactivity and structural similarities to the corresponding monomers.

4.3.4 Surfactant

Surfactant additives are used to lower the surface tension of the UV NIL resist so that its adhesion to the master mold after imprinting is reduced accordingly and a clean separation can be managed \[^{216}\]. Clearly, such surface-activating molecules must contain hydrophobic groups at the tails or branches for surface tension control. At the same time, they should be partly lipophilic with the backbones architectures similar to the diluent liquids.

Although fluorinated additives with medium chain lengths (8 - 12) \[^{217}\] are commonly used to reduce surface tension, they have the similar disadvantages of increasing the solution’s tendency to foam, especially when the weight ratio goes beyond 0.25%.
Therefore, silicone-containing surface additives are selected instead for better wetting and defoaming, improved surface slip and scratch resistance. The silicone surfactants\textsuperscript{[218-219]} are all variants of basic short-chain polydimethylsiloxane (PDMS) structure: \( \text{CH}_3[\text{Si(CH}_3\text{)}_2\text{O}]_n\text{Si(CH}_3\text{)}_3 \), because its non-polar and dimethyl-rich backbone can effectively lower the surface tension. Further modification of polarity degree is done by decorating a polyester chain on each silicone molecule and engineering the ratio of polyethylene oxide (PO) groups, because polar PO groups are very hydrophilic\textsuperscript{[220]}.

Normal silicone additives lack reactivity, and isn’t incorporated into the polymer binder network after polymerization. However, the performance expectations of UV resist on mechanical stability desire the formation of a fully cross-linked co-polymer structure without standalone molecules. To better serve this goal, silicone additives should be equipped with UV reactive groups compatible to those of POSS monomer hosts. For example, (meth)acrylate groups with double bonds are suitable to free-radical POSS monomers, and epoxy groups are for ring-opening POSS monomers.

Taken all factors above into consideration, solution of 70% polyester-modified, multi-acrylic functional polydimethylsiloxane (PDMS) in propoxylated neopentyl glycol diacrylate (PONPGDA) is chosen as the surfactant in free-radical POSS resist system. For ring-opening POSS resist system, a solvent-free epoxy silicone (TEGO RC 1403, Evonik Industries) is used as the surfactant.
4.4 POSS UV NIL resist preparation

4.4.1 Free-radical POSS resist

Table 4.3 10% free-radical POSS resist system

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical Name</th>
<th>Weight Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>Methacryl POSS</td>
<td>10%</td>
</tr>
<tr>
<td>Diluent</td>
<td>Isobutyl methacrylate</td>
<td>88.75%</td>
</tr>
<tr>
<td>Photoinitiator</td>
<td>2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl)-1-butanone</td>
<td>1%</td>
</tr>
<tr>
<td>Surfactant</td>
<td>70% polyester-modified, multi-acrylic functional polydimethylsiloxane in propoxylated neopentyl glycol diacrylate</td>
<td>0.25%</td>
</tr>
</tbody>
</table>

Combining the material selections on each individual component, Table 4.3 lists the recipe of 10% free-radical POSS resist system. The diluent isobutyl methacrylate is normally stored at 4 °C, so the diluent container should be placed at room temperature for 30 min before use to avoid moisture absorption. All components of total 100 g are then mixed in a 120 ml Boston round amber glass solution bottle in order, vigorously stirred for 12 hours at room temperature, and filtered with 0.2 μm-pore PTFE filter. The solution container should be stored at room temperature and kept away from direct exposure to light.
4.4.2 Ring-opening POSS resist

Table 4.4 10% ring-opening POSS resist system

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical Name</th>
<th>Weight Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>POSS</td>
<td>10%</td>
</tr>
<tr>
<td>Diluent</td>
<td>Neopentyl glycol di-glycidyl ether</td>
<td>88.5%</td>
</tr>
<tr>
<td>Photoinitiator</td>
<td>Mixed triarylsulfonium hexafluoroantimonate salts in propylene carbonate</td>
<td>1%</td>
</tr>
<tr>
<td>Photosensitizer</td>
<td>Isopropyl thioxanthone (ITX)</td>
<td>0.25%</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Epoxy silicone</td>
<td>0.25%</td>
</tr>
</tbody>
</table>

Table 4.4 lists the recipe of 10% ring-opening POSS resist system. The diluent neopentyl glycol di-glycidyl ether should be stored at 4 °C, so the diluent container needs to be placed at room temperature for 30 min before use to avoid moisture absorption. All components of total 100 g are then mixed in a 120 ml Boston round amber glass solution bottle in order, vigorously stirred for 12 hours at room temperature, and filtered with 0.2 μm-pore PTFE filter. The solution container should be stored at room temperature and kept away from direct exposure to light.
4.5 Resist properties

To compare the properties among two POSS resist systems and commercial resist (NXR-2030, Nanonex), these three solutions (10%) were coated on individual 2-inch Si test wafers at 4000 rpm, respectively, and each film thickness was recorded with the ellipsometer. The UV curing was performed under a UV spot-lamp system (BlueWave 200, Bymax, 40 W/cm² in 280-450 nm) for 30 s. The water contact angle test and RIE rate tests with different etching recipes were then conducted on every photocured sample surface. Table 4.5 summarizes the comparison results in different categories:

Table 4.5 Property comparison on SSQ resist systems and commercial resist

<table>
<thead>
<tr>
<th></th>
<th>Ring-opening POSS (10%)</th>
<th>Free-radical POSS (10%)</th>
<th>NXR-2030 (10%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxygen Inhibition</strong></td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Thickness</strong></td>
<td>156 nm</td>
<td>142 nm</td>
<td>146 nm</td>
</tr>
<tr>
<td>(4000 rpm, on Si)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Shrinkage</strong></td>
<td>4.9%</td>
<td>5.6%</td>
<td>12.6%</td>
</tr>
<tr>
<td><strong>Water Contact Angle</strong></td>
<td>95°</td>
<td>93°</td>
<td>93°</td>
</tr>
<tr>
<td><strong>RIE rate in O₂</strong></td>
<td>3.1 nm/min</td>
<td>3.3 nm/min</td>
<td>4.2 nm/min</td>
</tr>
<tr>
<td><strong>RIE rate in SiO₂ recipe</strong></td>
<td>27 nm/min</td>
<td>30 nm/min</td>
<td>36 nm/min</td>
</tr>
<tr>
<td>(SiO₂: 60nm/min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>RIE rate in Si recipe</strong></td>
<td>23 nm/min</td>
<td>25 nm/min</td>
<td>35 nm/min</td>
</tr>
<tr>
<td>(Si: 25nm/min)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The water contact angles on all three samples are all in 90° - 95° range, showing moderate hydrophobic surface properties. The similarity in contact angles are greatly due to the use of PDMS-type surfactants with the same concentration (0.25%), and such concentration level is also the best balance between good film formation and lower surface adhesion.

The volumetric shrinkage test upon polymerization is performed by filling each solution into a straight PTFE capillary tubing (1.8 mm O.D. × 0.5 mm I.D.) and measuring the initial liquid filling length \( l_0 \). After the UV curing, the remaining polymer filling length \( l_1 \) is measured, and the value \( \frac{l_0 - l_1}{l_0} \times 100 \) presents the calculated volumetric shrinkage. The results demonstrate great improvements (> 55%) on patterning fidelity of POSS systems compared to NXR-2030, because the superior cage architecture provide less compression and deformation scales than the linear PDMS-type architecture of NXR-2030. A higher POSS monomer can further reduce the shrinkage but the coating thickness is also dramatically increased, so a trade-off is reached to balance the pattern fidelity and thin residue imprinting.

RIE rate test results in oxygen (1 mtorr, 10 sccm, 50W) indicate these resist materials have strong etching resistance because of their Si-rich molecular architectures. Extra long-term (10 min) oxygen RIEs confirmed that all resist etchings stopped after removing initial 10-15 nm top surface, which means the well exposed Si-O interface blocks the reactive oxygen particles. Both POSS systems also show 21% - 26% RIE rate reduction, compared with the rate from PDMS-type NXR-2030 resist, and this may be attribute to the dense silica-type cage core of POSS.
RIE test results in SiO$_2$ recipe (CF$_4$/H$_2$, 33/7 sccm, 50 mtorr, 300 W) demonstrate the good etching selectivity to dry oxidation SiO$_2$. 0.45 – 0.5 vertical etching selectivity means the cured 150 nm-thick POSS film will theoretically support up to 300nm SiO$_2$ pattern transfer, and this is sufficient for most nanophotonic device layer on SiO$_2$. 0.92 to 1 etching selectivity to Si in a particular recipe (CHF$_3$/O$_2$, 10/2 sccm, 10 mtorr, 100W) is also achieved by two POSS system, which shows an average 30% selectivity improvement to that of NXR-2030. Compared with the SiO$_2$ RIE recipe, Si recipe contains a combination of fluorinated gas and oxygen, which are more effective to remove fused silica inner core structures and organic outer shells of POSS. Therefore, the selectivity to Si won’t match that to SiO$_2$, but it is still considerably improved over NXR-2030 due to dense 3D cage networks.

4.6 Imprint with free-radical POSS system

4.6.1 Bi-layer stack with PVA sub-layer for pattern transfer

The free-radical POSS system provides great performances upon polymerization, such as good etching selectivity to common substrates and ideal stability in harsh organic solvents, so that the patterned POSS can be naturally used as the etching mask or final device structures. However, its robustness also presents a difficulty in removing POSS layer from the substrate when direct substrate etching or Cr mask transfer is completed, with regular dry RIE or lift-off. A bi-layer stack is designed to facilitate such processes without compromising original POSS performances.
The key idea of a bi-layer stack approach is to include a specific polymer sub-layer between POSS resist layer and the substrate. Such a sub-layer material should meet the following criteria: (1) Strong adhesion to both the substrate and the POSS materials; (2) Good solubility in moderate solvents; (3) High etching rate in a particular RIE recipe, which shows a negligible etching effect on POSS material. (4) Ideal coating formation on the substrate with tunable thickness control.

**Figure 4.6 General bi-layer UV NIL method:** (a) imprint of UV resist on sub-layer, (b) two-step RIE of pattern transfer, (c) functional material deposition, and (d) lift-off of bi-layer

Using a polymer material with such characteristics, the bi-layer stack provides the following general pattern transfer method (Figure 4.6): (1) The POSS resist is first patterned with UV NIL based on HiF2M (Figure 4.6a), and an RIE process to remove the thin residue and expose the sub-layer. At the same time, an over etching can be introduced to expand the pattern lateral dimensions in a controllable manner. (2) The second RIE with a different gas combination is adopted to etch through the sub-layer...
until the substrate surface, leaving POSS patterns intact (Figure 4.6b). (3) Functional material layer such as a Cr mask layer or Au plasmonic feature layer is deposited onto the substrate (Figure 4.6c), and a simple lift-off will remove the entire material stack (Figure 4.6d). The sample is then used as it is or performing the future processes.

To better work with POSS system, poly(vinyl alcohol) (PVA, or PVOH) solution in DI water is used and evaluated. PVA is a white non-toxic synthetic polymer with the formula of \([\text{CH}_2\text{CH(OH)}]_n\) \(^{[224-225]}\), which presents the following ideal properties: (1) great adhesion without corrosion to most substrates including Si, SiO\(_2\), metal and plastics; (2) good water solubility and resistant to oil and solvents at the same time; It means POSS coating can be safely coated on the PVA layer which should be easily removed by rinsing in water afterwards. (3) high etching rate (58 nm/min) in oxygen RIE (1 mtorr, 10 sccm, 50W) which won’t affect POSS patterns; (4) excellent film forming property with controllable thickness by adjusting PVA concentrations; (5) High strength and close to incompressible.

Even through PVA can provides superior adhesion to diverse substrates with intermolecular forces, a special additive is adopted to further enhance the adhesion between POSS resist and PVA layers by providing robust chemical bonding capabilities. Ethoxylated trimethylolpropane triacrylate is a free-radical UV monomer material with 5% water solubility at room temperature. Its existing in PVA solution grants a strong chemical bonding (C-C bonds) formation to POSS resist only at the interface with photoinitiator supplied by the resist, and the bulk PVA layer still remains water soluble after UV curing. Its Si-free formula makes it completely compatible to the PVA etching method in oxygen RIE.
PVA is supplied in powder form (Sigma Aldrich, Mw 31,000-50,000, 98-99% hydrolyzed) and a 5% solution is made from it: (1) 4.9 g PVA powder with 0.1 g ethoxylated trimethylolpropane triacrylate are first slowly added to 95g DI water at 4°C to reduce formation of lumps. (2) The mixture is heated to maintained at 95°C for 6 hours until PVA solid becomes fully solubilized. (3) The mixture is gradually cooled down to room temperature. Such PVA solution provides 80 nm coating thickness at 3000 rpm spinning, and a higher thickness can be achieved by increasing PVA concentration.

4.6.2 UV NIL in free-radical POSS and Cr mask transfer

Figure 4.7 Imprinted free-radical POSS resist with bi-layer stack on Si substrate, using a 135 µm-pitch pillar array HiF2M.
Based on the previously discussed bi-layer stack approach. A 80 nm-thick solid PVA sub-layer is first formed on the target substrate by spinning 5% PVA solution at 3000 rpm for 60 s and baking it at 120ºC for 5 min. A 145 nm-thick resist layer is then coated with 10% free-radical POSS solution at 8000 rpm and attached with a designated HiF2M mold. A UV NIL process is performed at 40 Psi for 10 s to cure the resist, and HiF2M is separated from the sample. Figure 4.7 shows the result of imprinting a 135 µm-pitch pillar HiF2M onto the free-radical POSS, and a uniform 45 nm-wide hole array is formed with the demonstrations of high resolution, high fidelity and stable adhesion of PVA to the Si substrate and POSS layer.

![Figure 4.7 Imprinted POSS pattern](image)

**Figure 4.8 Transferred Cr mask pads with different POSS residue etching durations.**

In order to further transfer a Cr mask layer to the substrate, a two-step RIE process first removes POSS residue in pattern features using CHF$_3$/O$_2$ (10 mTorr, 10/2 sccm, 100W) with a minimum 1 min duration, and then a pure O$_2$ RIE (1 mTorr, 10 sccm, 50W) of 5 min exposes the substrate by etching though PVA sub-layer. 10 nm-thick Cr E-beam evaporation deposited the mask layer onto the substrate and a throughout ultrasonic cleaning in water removes the resist stack. Such two-step RIE not only opens the pathway for Cr mask deposition, but also provides a convenient way to control the final Cr feature...
dimensions by over etching with different durations. Figure 4.8 demonstrates this feasible idea showing the Cr pad diameters with different POSS etching durations. With a 1 min etching, the result shows a 45 nm-diameter Cr pad corresponding to the original POSS pattern diameter, therefore presents a high-fidelity pattern transfer with no detectable lateral dimension expansion. By increasing the RIE duration, Cr pads with larger diameters can be acquired. A linear relation with 20 nm/min lateral expansion rate can be calculated by fitting the data exacted from all images. This predictable expansion behavior provides a control mechanism to deliver modified feature dimensions from the same imprinting conditions without the need of different master molds, and it will greatly reduce the design complexity and time cost for device prototyping and optimization which need to quickly evaluate devices with chosen lateral dimensions.

Using the bi-layer stack, Cr masks can be transferred to diverse substrates. These substrates include regular Si-type materials (Si, thermal SiO₂, fused silica), sapphire, metals (Au, Al and stainless steel), III-V materials (InP), thermal plastics (PET) and soft elastomer (PDMS).
The ideal adhesion makes PVA compatible to such different substrate types without the need of extra adhesion promoter, and a brief oxygen plasma cleaning of the target substrate prior to coating is always a good pre-treatment step. Flexible HiF2M facilities the separation, offering patterning on extremely rigid substrates like sapphire an improved handling experience without little locking (Figure 4.9a). The great film formation and reflow performances of PVA creates a smoother surface for resist dispersion on coarse substrates like ZnO grains (Figure 4.9b) and mechanically polished stainless steel plates with surface roughness up to 200 nm. PVA water solubility gives a safe and clean way to perform the lift-off with without harsh solvents, and it is essentially compatible to the applications on chemical sensitive substrates like PDMS. All these capabilities lay the foundations of large-area, high-yield and uniform imprinting on POSS top layers.
4.6.3 Metal MESH fabrication by bi-layer stack

One important application of bi-layer resist stack is the fabrication of 200 nm-pith Au metal-mesh electrode with subwavelength hole-array (MESH) structures. MESH is typically a gold hole array of 175 nm diameter, 200 nm pitch and no more than 30 nm thickness as transparent electrode on a fused silica substrate to replace ITO (Figure 4.10). Compared with a 100 nm-thick ITO film, MESH presents a much smaller (> 4.5 fold) sheet resistance, reduced reflection and absorption in the most visible range. Based upon MESH structures, diverse plasmonic cavity with subwavelength hole-array (PlaCSH) devices were built and tested: (1) PlaCSH solar cell has achieved up to 96% light coupling efficiency, broad-band and Omni acceptance, 69% external quantum efficiency and 4.4% power conversion efficiency (PCE) [66]. (2) Compared with conventional organic LED (OLED) structure, PlaCSH OLED exhibits 1.57-fold higher external quantum efficiency and light-extraction efficiency, 2.5-fold higher ambient light absorption with broad-band (400 nm), angle and polarization independent properties, 1.86-fold higher normal view brightness and uniform color over all emission angles [65]. All performances above are due to the truth that PlaCSH is an excellent optical antenna with excellent radiation and absorption of light. Also, MESH is a simple architecture to fabricate with NIL in a large-area and high-through way.
Figure 4.10 Plasmonic cavity with subwavelength hole array (PlaCSH) solar cell structure with integrated MESH layer as anode [66].

Originally, Au MESH fabrication was done by thermal NIL in a single-layer resist on a fused silica substrate, followed by residue etching, Au deposition and lift-off. There are three major disadvantages to use this approach as a universal method on diverse substrates: (1) The single-layer patterning restricts its maximum Au deposition thickness tolerance in order to perform a successful lift-off, because the successive residue etching process right after NIL generally deteriorates the resist patterning contrast in terms of height and side wall angle; (2) High pressure (250 Psi) introduces dense surface charges at the mold-resist interface especially in the case of fused silica substrate, and greatly increases separation difficulties; (3) High temperature (130 ºC) is not suitable for potential thermal plastic substrates since they have large coefficients of thermal expansion (CTE) which compromise the patterning fidelity in pitch and feature size. Therefore, a fabrication approach with room temperature, moderate pressure and
improved lift-off structures is demand for this mission. The UV NIL with HiF2M and bi-layer resist stack is a natural choice.

Figure 4.11 Au MESH fabrication with HiF2M and POSS bi-layer stack: (A) One-step roller NIL with 200 nm-pitch hole array HiF2M patterns POSS pillars on PET film with PVA sub-layer, (B) two-step RIE isolates the bi-layer pillars as the evaporation mask, (C) Au E-beam evaporation transfers a uniform thin Au MESH on PET, and (D) Simple lift-off in DI water leaves clean MESH.

Au MESH fabrication using bi-layer POSS stack includes four major steps, and Figure 4.11 shows the SEM cross-section result of each step in building a 50 nm-thick Au MESH layer:
(1) 145 nm-thick PVA sub-layer is coated on the substrate, followed by an 80 nm-thick POSS resist spinning. The stack is UV imprinted with a 200 nm-pitch and 130 nm-diameter HiF2M hole mold at 40 Psi and room temperature. After NIL, the inversed POSS resist pillar array is made on top of the intact PVA sub-layer with 110 nm initial height. The cross-section detail in Figure 4.11a confirms the pillar formation with less than 10 nm residual layer due to the low viscosity of POSS resist, and this greatly reduces the impact of incoming RIE process to pillar lateral dimension by minimizing the duration for complete residue removal.

(2) PVA sub-layer is exposed by etching away POSS residual layer in a short-duration RIE (CHF$_3$/O$_2$, 10/2 sccm, 10 mTorr, 100W, 30 s), and then etched through to the substrate using O$_2$ RIE (1 mTorr, 10 sccm, 50W, 5 min). Figure 4.11b shows isolated bi-layer pillars with remaining 100 nm-thick POSS caps and full-thickness PVA bases. Thanks to the excellent etching resistance in oxygen RIE, POSS patterns well protected the underneath PVA and shape the straight side walls of pillars with an aspect ratio of 2, and 60% of the total height belongs to water-soluble PVA.

(3) 2 nm-thick Ti for adhesion promotion and 50 nm-thick Au for MESH formation are deposited with two consecutive E-beam evaporations, and a continuous 200 nm-pitch MESH layer is created on the substrate (Figure 4.11c). The straight bi-layer pillar side walls help to reduce Au diffusion, and a total 50 nm-thick PVA section is still exposed after the 50 nm Au evaporation, and it is absolutely sufficient for lift-off. PVA thickness can be easily tuned based on the following functional material deposition such as Au and Cr without changing other major
step parameters, so it offers a universal adaptive approach to generate lift-off friendly resist patterns with high aspect ratios, using the extra same master mold.

(4) The clean MESH film on substrate is acquired by performing the lift-off with ultrasonic DI water cleaning process for 5 min (Figure 4.11d). No special solvents are needed, and it eliminates the risk of any compatibility issue with bi-layer materials and damage to potential fragile substrates like PDMS.

![Roller mold with 170nm hole patterns](image1.png) ![20nm-thick Au MESH on PET film](image2.png)

**Figure 4.12** (a) HiF2M mold of 200 nm pitch and 170 nm diameter holes for roller UV NIL, and (b) 20 nm-thick Au MESH on 175 µm-thick PET film after pattern transfer through POSS bi-layer stack.

Based on the same procedure, MESH on PET is made by roller UV NIL for specific applications in flexible solar cells and OLEDs. HiF2M roller mold with average 172.4 nm hole diameter (Figure 4.12a) is duplicated from a polymer master mold, and imprinted into an 80/80 nm bi-layer POSS stack coated on 125 µm-thick PET film. The fabricated MESH has an average 170.7 diameter, with 99.0% transfer fidelity (Figure 4.12b). Roller UV NIL also opens a path for potential large-area continuous fabrication
of MESH: in the pilot tests, 2 × 3 inch² MESH on PET samples can be made with >95% overall yield (Figure 4.13a). The sample size is defined by the size of identical HiF2M molds attached to the roller, so the fabrication throughout can be further improved by adopting larger HiF2M units. Built upon the MESH sample, functionalized PlaCSH solar cells are made with MESH anodes (Figure 4.13b), and the preliminary performance tests show the similar results close to MESH on fused silica devices.

![Figure 4.13](image)

**Figure 4.13 (a)** 20 nm-thick Au MESH on PET film made by roller UV NIL, and **(b)** Fully-built PlaCSH solar cell on PET with integrated MESH layer as the anode.

### 4.7 Imprint with ring-opening POSS system

The most significant advantage of ring-opening POSS system is the truth that its UV curing mechanism has no problem in the presence of oxygen, and this is the very foundation that ring-opening POSS system can be used in an open and continuous fabrication setup such as a roller NIL machine. On the other hand, ring-opening POSS lacks of a matched sub-layer material candidate due to relatively weak film forming
capabilities on regular water-soluble polymer materials. Therefore, the best scenario for ring-opening POSS system is direct single-layer UV NIL patterning on Si-type or PET substrate with the help of adhesion promoting middle layer.

### 4.7.1 Direct dielectric nanopattern formation with high fidelity

Despite of a different curing mechanism from free-radical POSS system, ring-opening POSS system has the almost identical excellent properties of high stiffness, ideal chemical stability and low volumetric shrinkage, which are determined by its stable and dense fused silica cage architecture. Therefore, direct UV patterning of ring-opening POSS resist and using of the patterned polymer nanostructures as a good replacing dielectric material of conventional ones like SiO₂ is a feasible direction to many potential applications.

**Figure 4.14 HiF2M fabrication by direct casting and inversion of the rigid master mold:** (a) the master mold with patterned SiO₂ pillars, and its surface has been treatment with surfactant to lower the surface tension, (b) direct PFPE coating on the master mold and curing, and (c) PFPE HiF2M separation.

To generate final polymer nanopatterns identical to the master mold with high fidelity, PFPE pre-polymer solution is directly coated on the master mold (Figure 4.14a), pressed
to a 175 µm-thick PET film (Melinex ST 504, DuPont) and UV cured (Figure 4.14b), so that the corresponding HiF2M can faithfully inverse the master mold features with previously demonstrated accuracy (Figure 4.14c). The master mold surface is modified with the surfactant (NXR-10, Nanonex) to acquire a low surface tension state with 110º water contact angle which facilitates HiF2M separation from the master mold. Melinex ST 504 PET product provides a thin adhesion promotor layer pre-coated on one side of the PET film, and it exhibits a sufficient bonding strength that previously used epoxy adhesive layer can be completed replaced to greatly simplify the HiF2M fabrication time and structural complexity.

To test the overall transfer fidelity, a SiO₂ master mold with a pillar array of 200 nm pitch, 87 nm average diameter and 62.7 nm average height was used to duplicate an inverted HiF2M mold. The HiF2M mold was then adopted in UV NIL of ring-opening POSS resist to create a full polymer pillar array on Si substrate. Figure 4.15 shows the AFM inspection results of each individual components: master mold, HiF2M mold, and POSS sample. The final POSS pillar array exhibits an average height of 60.9 nm, and its corresponding to 97.1% transfer fidelity in vertical height compared to the master mold, and a followed SEM inspection of lateral pattern dimensions show a similar fidelity value at 97.0%. These are attributed to the high-fidelity duplication of HiF2M and the low volumetric shrinkage of ring-opening POSS. AFM investigations also confirm that pattern POSS pillars have the flat top surfaces and sharp side wall profiles closely like the master SiO₂ pillars, and it is due to low viscosity POSS flowing and filling capability and high stiffness after polymerization. The combination of the high-fidelity performances
from HiF2M fabrication and POSS UV NIL delivers an overall ring-opening resist nanopatterns with almost identical features to its master.

**Figure 4.15** AFM inspections to evaluate transferring pattern fidelity in direct POSS patterning: (a) SiO₂ pillar master mold of 200 nm pitch, (b) inversed PFPE HiF2M hole mold, (c) imprinted ring-opening POSS resist pillar arrays.

### 4.7.2 D2PA fabrication with direct formation of POSS patterns

One straightforward application of direct POSS pattern formation is the fabrication of polymer D2PA. Disk-coupled dots-on-pillar antenna (D2PA) structure \(^{[63]}\) (Figure 4.16) combines high-density three-dimensional cavity nanoantennas built with a metal disk
array and backplane on the top and the foot of SiO$_2$ pillars, respectively. These nanoantennas are then coupled to even denser plasmonic metal nanodots on SiO$_2$ pillar side walls in the cavities. This unique structure and its variants demonstrated (1) an area-average SERS enhancement of $1.2 \times 10^9$ and large-area uniformity with the variation of less than 25%; (2) An average fluorescence of an infrared dye is enhanced by 2970 fold with less than 11% uniformity variation over a large sample area and over a wide range of dye concentrations [226]. (3) An average fluorescence enhancement of an immunoassay of protein A and human immunoglobulin (IgG) by over 7400-fold and the detection sensitivity by $3 \times 10^6$-fold, compared to identical assays performed on flat glass plates [227].

Figure 4.16 Disk-coupled dots-on-pillar antenna (D2PA) structure. (a) schematics; (b) top-view scanning electron micrograph; and (c) cross-sectional SEM of a D2PA structure, consisting of dense 3D cavity antennas coupled to dense Au nanodots in cavity gaps [63].
Although SiO$_2$ D2PA structures present world-record performances, the fabrication procedure is relatively complex and time-consuming, and it demands precise parameter controls due to its low tolerance to pillar dimension variations. In order to generate the designated SiO$_2$ pillar geometry parameters, two precise RIEs are needed to deliver Cr mask with required diameter, and to etched down the SiO$_2$ layer with certain depth, respectively. Only ±1 nm variation is allowed to achieved qualified performances in a repeatable way, and large-area uniformity over a 4-inch wafer substrate puts more requirements on accuracy controls.

**Figure 4.17** Polymer D2PA fabrication on PET with direct pillar formation of ring-opening POSS resist: (a) one-step roller NIL creates POSS polymer pillar array of 200 nm pitch, (b) Normal Au evaporation generates top Au disks, sidewall nanodots, and backplane with self-alignment.

High-fidelity direct patterning with ring-opening POSS resist proposes a solution to this issue by forming POSS pillar array in single one-step NIL process, and POSS
structures have comparable performances to SiO$_2$ in terms of mechanical strength and chemical stability. First, a HiF2M mold is inversely replicated from a pillar SiO$_2$ master mold with the exactly same pillar dimensions in real D2PA structures. The verified high-fidelity HiF2M mold fabrication will loyally record the pillar dimension information into the complementary PFPE patterns on top of the HiF2M mold. Next, 156 nm-thick ring-opening POSS is coated on PET film with a 6 nm-thick adhesion promoter layer (ST-12, Nanonex) in the middle, and UV imprinted with the HiF2M mold. POSS pillar array transferred by high-fidelity imprinting into low-shrinkage POSS material is formed on PET (Figure 4.17a), with 97.1% feature duplication accuracy to the original SiO$_2$ mold. Finally, a Ti/Au (1.5/52 nm) E-beam evaporation completes the D2PA formation by generating the top Au disks, backplane and nanodots on POSS pillar side walls at the same time, in a self-alignment manner (Figure 4.17b). The entire procedure uses neither RIE etchings nor Cr mask deposition, which tremendously simplifies the fabrication complexity, suppresses sources of parameter variations, and reduces the total fabrication duration by 5 hours.

4.8 Summary

To address the existing issues of current resists systems with high volumetric shrinkage, oxygen inhibition, large monomer weight variation, limited etching selectivity and so on. Two UV resist systems based on small-molecule POSS monomers were designed, engineered and tested, and both systems show advantages like (1) good surface tension with generally hydrophobic wetting, (2) improvement on oxygen resistance by adopting more efficient photoinitiator in free-radical system, or using catatonic
polymerization mechanism which takes on effect from oxygen, (3) reduced volumetric shrinkage to 5% and lower, (4) great RIE selectivity due to the unique dense 3D cage architecture, (5) ideal chemical stability and so on. Based on the bi-layer stack of free-radical POSS resist system and supporting PVA sub-layer, functional material patterns can be transferred to assorted substrates with great differences in material types, stiffness and roughness in a simple UV NIL and two-step RIE process combination. Also, such bi-layer architecture provides control to modify lateral dimensions of post-imprinting patterns for fast device structure optimization. For ring-opening POSS resist system, high-fidelity directly-imprinted POSS patterns show the potentials as an alternative to regular SiO$_2$ patterning material with greatly simplified device fabrication procedure.
Chapter 5

Transfer Printing of Metallic Nanostructures

5.1 Introduction

Although nanoimprint lithography generally provides a low-cost, high-throughput, and high-resolution nanofabrication process, it demands a surface with the proper wetting and topological properties to create a uniform resist coating. In order to remove the patterned resist mask, harsh organic solvents like acetone are applied, and the substrate has to be chemically stable in the lift-off process. These factors put the limitations when nanostructures need to be built on soft, chemical sensitive and/or patterned substrates.

Transferring metallic nanostructures onto target substrates with patterned molds [228-232] is an interesting unconventional nanofabrication method. When a metallic material deposition is performed on a patterned mold surface, a thin layer of self-aligned and confined metal patterns is formed on the top surface of the mold, which can be transferred to receiving substrate in one step by pressing the mold on to it with proper surface pre-modification in a chemical or physical way. The promising applications of the metallic structures as high-performance electrodes and plasmonic antenna devices [231,
Several factors \cite{235-237} determine the yield of the metallic nanostructure transfer: (1) master pattern resolutions. (2) properties of the transfer metallic materials. (3) adhesion strength between the metallic materials and the target substrate. Given a specific metal type to be transferred, corresponding master mold materials need to be deliberately selected with a sufficient stiffness to support the designated resolution, and a proper surface tension to improve the metal film integrity and facilitate the final separation. Besides soft PDMS, several types of polymers have been used as the master mold materials due to the highly-tunable, low-cost and easy-fabrication natures.

In this chapter, we will introduce our approach by using a patterned flexible mold of modified hard PDMS to transfer 200 nm-pitch metal MESH layers onto various substrates, including hard materials like Si and GaAs, typical thermal plastics like PMMA and PS, and unconventional materials like conductive polymers and soft PDMS. We will also demonstrate the successful one-step transfer printing of an entire 50 nm-thick Au MESH layer onto a 4-inch Si wafers with pre-patterned trenches with up to 20 µm width.

5.2 Modified hard PDMS mold for transfer printing

5.2.1 Mold materials
Table 5.1 Modified hard PDMS materials

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical Name</th>
<th>Weight Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear vinyl siloxane</td>
<td>7.5% reactive methyl-vinyl-siloxane groups in the siloxane chain</td>
<td>40.4%</td>
</tr>
<tr>
<td>Linear hydride siloxane</td>
<td>27.5% reactive methyl-hydride-siloxane groups in the siloxane chain</td>
<td>32.3%</td>
</tr>
<tr>
<td>Vinyl Q-siloxane</td>
<td>50% solution of vinyl Q-siloxanes in xylene</td>
<td>24.2%</td>
</tr>
<tr>
<td>Platinum catalyst</td>
<td>3% platinum di-vinyl-tetra-methyl-di-siloxane in xylene</td>
<td>0.4%</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>2,4,6,8-tetra-vinyl-2,4,6,8-tetra-methyl-cyclo-tetra-siloxane</td>
<td>2.7%</td>
</tr>
</tbody>
</table>

The modified hard PDMS (h-PDMS) materials used in the master molds of transfer printing are the direct modification of the typical hard PDMS recipe.

Table 5.1 shows the comprehensive list of materials to prepare the modified PDMS pre-polymers. In the original h-PDMS materials \(^{[145]}\), only linear base siloxane molecules with separate vinyl and hydride functional groups were used to form the polymer network upon polymerization, which limited its stiffness to a maximum 9 MPa. A novel approach was adopted to further increase the PDMS Young’s modulus by adding a branched siloxane component as cross-linkers \(^{[238]}\). Each cross-linker molecule in the network created multiple linking bonds in different three-dimensional directions, which greatly increased the link density and boosted the final stiffness. The platinum catalyst assisted
the polymerization reaction among siloxane molecules, and the inhibitor controlled the reaction rate in the moderate curing temperature and permitted enough time to handle the mixed pre-polymers in processed like spin-coating and de-gassing. The final PDMS stiffness is highly determined by the relative weight ratios of these siloxane molecules. The listed weight ratios in

Table 5.1 generated the PDMS polymer with Young’s modulus around 72 MPa which is sufficient to support sub-50 nm mold feature resolution in the followed experiments.

**Figure 5.1 Preparation of modified hard PDMS pre-polymer and curing recipe**

Figure 5.1 illustrates the complete flow of modified h-PDMS pre-polymer and h-PDMS polymerization process. It starts from mixing 3 g of vinyl linear siloxane (VDT-731, Gelest) and 2.4 g of vinyl Q-siloxane (VDX-221, Gelest) in a 10 ml clear glass bottle. The xylene solvent is evaporated from the solution in a 25” Hg vacuum oven at 60°C for 24 hours. After the solution is cooled down to the room temperature, 0.2g of inhibitor (87927, Sigma) is added to the solution and thoroughly stirred. 30 µL of platinum catalyst (SIP6831.1, Gelest) is added next and stirred. The inhibitor creates a
buffered environment in the solution which allows the catalyst droplet to be well mixed before stimulating excessive local polymerization to impact the pre-polymer viscosity. 1.8g of hydride linear siloxane (HMS-501, Gelest) is then mixed with the solution and de-gassed in 25” Hg vacuum in the room temperature for 5 minutes. The pre-polymer is now ready to be applied to the target substrate for molding, and it can be fully cured by be placed in 25” Hg vacuum oven at 45°C for 24 hours.

5.2.2 Mold fabrication process

![Mold fabrication process diagram]

Figure 5.2 Fabrication of modified h-PDMS mold for transfer printing

Based on the systematic research on flexible PFPE mold fabrication, a similar large-area approach was successfully performed (Figure 5.2). A pre-imprinted thermal NIL resist layer (NP69, Nanonex) on a 4-inch Si wafer serves as the master mold. As a high-performance thermal NIL resist product, NP69 features sub-10 nm theoretical resolution,
wafer-scale uniformity and ideal stability at room temperature, which makes it capable of carrying and transferring designated nanometer-scale patterning information.

2 mL of the prepared h-PDMS pre-polymer solution is dropped onto a patterned master mold of NP69, and the spin coating is performed at 1500 rpm for 60 seconds. The coated mold is placed into a 25” Hg vacuum oven at 45°C for 24 hours to fully cure the h-PDMS layer and replicated the patterns from the master mold. Upon the polymerization, the master mold is cooled down in the atmosphere for next steps. At the same time, a batch of soft PDMS pre-polymer solution is made by mixing 5 g of the base and 0.5 g of the cross-linker, and de-gasses for 30 minutes. 2 mL of soft PDMS pre-polymer is applied to the master mold by spin coating at 1500 rpm for 60 seconds, and then carefully covered with a 175 µm-thick PET film as the backplane of the flexible mold. To form a secure bonding between the soft PDMS layer and the PET film, the PET film can be exposed to a brief O₂ RIE process with 50 mTorr chamber pressure, 20 sccm flow rate and 75 W power for 90 seconds. The assembly is then loaded into the nanoimprinter (NX-2500, Nanonex) to be pressed at 5 Psi for 2 minutes, to remove trapped air and generate uniform soft-PDMS middle layer of the flexible mold. Finally, the entire assembly is sent into the 25” Hg vacuum oven to cure the soft PDMS layer for another 24 hours. After that, the h-PDMS flexible mold is separated from the master mold by peeling and stored properly for incoming metal depositions.

Using the modified h-PDMS material and the corresponding mod fabrication process, 200nm-pitch and 135 nm-diameter hold mold of transfer printing was successfully replicated from a NP69 master mold with inversed 200 nm-pitch pillar arrays (Figure 5.3). Due to the weak adhesion between NP69 and h-PDMS and the moderate stiffness of
the h-PDMS mold, the separation was able to be easily performed, without damaging the integrity of the master mold patterns, so the master molds can be re-used for multiple cycles. At the same time, large-area h-PDMS molds were fabricated featuring up to a 4-inch wafer area, and Figure 5.4 shows a modified h-PDMS mold with 1 µm-pitch pillar arrays and 4-inch wafer size.

![Image of SEM images of (a) 200 nm-pitch master mold patterns of NP69 and (b) fabricated h-PDMS mold patterns of 135 nm-diameter](image)

**Figure 5.3** SEM images of (a) 200 nm-pitch master mold patterns of NP69 and (b) fabricated h-PDMS mold patterns of 135 nm-diameter
5.3 Transfer printing of Au MESH layer with surface treatments

Two factors determine a successful transfer printing of metallic nanostructures: (1) flexible mold materials ensure metallic pattern resolution and film integrity, which both have been demonstrated by adopting modified h-PDMS as the patterning mold material; (2) An ideal substrate surface guarantees sufficient adhesion to the metallic layer during the separation phase. In this session, we demonstrated high-yield large-area transfer printings of Au MESH layers to target substrates by applying proper adhesion promoters to the substrate surfaces in advance (Figure 5.5). The Au deposited flexible mold is then pressed onto the substrate with a designated working pressure to assist the bonding process, and then separated to leave the intact Au MESH on the substrate.
5.3.1 Surface treatment for adhesion promotion

For the selected adhesion promoter, it should present sufficient bonding strengths to both the substrate and the deposited Au layer, and such candidates can be selected based on the availability of proper functional groups. Among those candidates, silane agents are extensively studied and available as synthesized chemical products.

The general silane molecule has a formula of R-(CH$_2$)$_n$-Si-X$_3$. X is a hydrolysable group typically alkoxy, acyloxy, halogen or amine$^{[239]}$, and it will form a reactive silanol group upon hydrolysis, which can condense with other silanol groups to form strong and stable siloxane linkages$^{[240-241]}$. This means stable covalent bonds can be formed with typically Si-rich substrates like Si, thermal SiO$_2$ and fused silica wafers, and it is the essential property for a usable adhesion promoter$^{[242]}$. The R group in the silane formula is a nonhydrolysable organic radical, so by a deliberate chemical engineering process, silane molecules can be installed designated R group to possess strong adhesion to Au.

The self-assembled monolayers (SAMs) of n-alkylthiols (RSH) on metals and metallic nanoparticles (strong bonding to Au$^{[243-245]}$ and Ag$^{[246-247]}$, weaker but still effective to Cu$^{[248]}$ and Ni$^{[249]}$) have been intensely studied, in which case a sulfur atom links the rest of the RSH molecule to the metal surface via a covalent bond, and the van der Waals forces among surrounding molecules stabilize the overall structures. Therefore, thiol group (-SH) is an ideal end group to serve as the metal linker group in the silane
molecule with the form of HS-(CH$_2$)$_n$-Si-X$_3$. Upon the consideration of agent availability and unit price, (3-mercaptopropyl)trimethoxysilane (MPTMS, Sigma) with the linear formula HS-(CH$_2$)$_3$-Si-(OCH$_3$)$_3$ was selected as the silane adhesion promoter, and it was used as the solution of 1:100 (by volume) MPTMS and 2-Propanol (IPA) in the substrate surface modification process.

The substrate surface treatment is performed in the following steps: First, the cleaned substrate (Si, SiO$_2$ or glass) is functionalized with hydroxyl groups by a brief oxygen plasma treatment in the RIE system (50 mTorr, 20 sccm, 75 W for 90 seconds). After an effective plasma treatment, the substrate surface needs to show a strong hydrophilic property with less than 4° contact angle of water. The MPTMS solution is then dispensed onto the treated substrate at the dose of 0.1 mL/inch$^2$ using a spin coating process at 1000 rpm for 40s, and the substrate is placed on a hotplate at 110°C for 10 min. The substrate is then ready to secure the deposited Au nanostructures from the mold.

5.3.2 Transfer printing to flat rigid substrates

50 nm-thick Au is directly deposited onto a fresh h-PDMS hole mold of 200 nm-pitch and 130 nm-diameter with an E-beam evaporation at the rate of 1.0 Å/s, to form a continuous Au MESH layer on the top of the mold. The mold is then placed in contact with the MPTMS-coated substrate, and loaded into the nanoimprinter (NX-2500, Nanonex) for transfer printing at a 250 Psi pressure and 90 °C for 10 min. When the substrate is cooled down to the room temperature, the mold is peeled off from the substrate and the Au MESH is transferred onto the substrate.
Figure 5.6 Images of (a) 50 nm-thick Au MESH transferred onto a Si substrate, and (b) the h-PDMS mold after the top Au MESH layer was transferred successfully

This transfer printing method shows the high-yield transfer with great film integrity and uniformity. Figure 5.6 shows 50 nm-thick Au MESH covered Si substrate with a smooth and uniform metallic surface without visible defects, which justified the ideal overall film quality and transfer yield. The same conclusion can also be drawn based on the image of the h-PDMS mold after Au MESH transfer with a uniform color distribution. The SEM inspections demonstrated the successful Au MESH transfer in the micro scale (Figure 5.7): The Au MESH is continuous on all directions without defects like cracks and wrinkles, and every hole showed a clean opening area without any Au particle originally deposited into the holes of the h-PDMS mold. The average MESH hole diameter is 128.3 nm, which is closed to the 130.2 nm average hole diameter of the h-PDMS mold, and it proved the great transfer resolution and fidelity.
Based on the same procedure, large-area transfer printings of Au MESH were successfully conducted on different Si-rich substrates of 4-inch wafer size including Si, thermal SiO$_2$ and fused silica. Figure 5.8 is a full-wafer transfer of 20 nm-thick Au MESH onto a 4-inch bare Si wafer. Overall the entire wafer area, transferred MESH layer showed great film integrity and uniformity. The secure bonding between Au and the substrate presented a total resistance to regular organic solvent rinsing like ethanol and 2-propanol, making the substrate qualified for following process built on top of it.
Figure 5.8 Full-wafer transfer of a 20 nm-thick Au MESH layer on a 4-inch Si wafer

5.3.3 Transfer printing to patterned rigid substrate

The demonstration of large-area and high-yield transfer printing of continuous and uniform Au MESH opened the possibility of transfer onto patterned rigid substrates, which would be utilized as a novel fabrication approach to construct suspended thin-film metallic nanostructures over the substrates to form mechanical channels and optical cavities for potential applications.

The test patterned substrates were prepared with conventional photolithography and RIE processes: 1.4 µm-thick AZ5214 positive photoresist was coated on a 4-inch Si
wafer, and patterned with MA-6 aligner (SUSS). After photoresist development, the remaining resist layer was used as the etching mask to in direct Si RIE etching into the substrate, with 25/10 sccm CHF$_3$/O$_2$ at 50 mTorr and 300W. The average Si etching was 25 nm/min and a total 200 nm-thick Si was removed from the exposed substrate areas. The etched Si wafer was thoroughly cleaned in fresh Piranha solution (H$_2$SO$_4$:H$_2$O$_2$ 3:1) at 120°C for 20 min to eliminate surface contaminations. After rinsing with DI water, the substrate was dried with N$_2$ and baked on a hotplate of 110 °C to remove surface moisture. The substrate was then activated by oxygen plasma and coated with MPTMS based on the same process used on the flat substrates. A higher Au deposition rate of 1.0 Å/s was taken in the E-beam evaporation to lower the impact of accumulated heating to the MESH integrity due to the intrinsic mismatch in coefficients of thermal expansion (CTE) between Au and h-PDMS. The high modulus of h-PDMS also helped to improve the film quality by reducing the mechanical film deformation into the recessed substrate area in the transfer phase.

Transfer printing tests were performed with the same type of h-PDMS hole molds as the ones in the transfers to flat substrates, but Au MESH of different deposition thicknesses were used to evaluated the impact to the MESH film integrity after the separation. It was found that only when the Au thickness was no less than 50nm, a continuous and flat MESH layer was able to be transferred onto the patterned Si substrates, otherwise only the MESH blocks on top of the rising parts of the substrates were able to be transferred and the suspended MESH blocks cracked away from the layer and left attached to the mold, due to the weak mechanical strength of the thin Au MESH layer.
Figure 5.9 SEM images of 50 nm-thick Au MESH of 130 nm-diameter transferred onto the Si substrate of grating arrays with 1.3 µm spacing and 200 nm-trench depth: (a) top view, (b) tilt view
With careful controls of the Au deposition and transfer parameters, 50 nm-thick Au MESH of 130nm-diameter were able to be transferred onto the Si substrate of grating arrays with 1.3 µm spacing and 200 nm trench depth (Figure 5.9). The transferred Au MESH demonstrated ideal film integrity and flatness. No deformations and cracks were observed on suspended MESH blocks. This proved the feasibility of one-step sealed cavity formation approach, and it opened the path to fabricate advanced plasmonic devices with complicated vertical stacking layers.

The robustness of transferred 50 nm-thick Au MESH was further tested on Si substrates with recessed patterns of different dimensions. The SEM investigation proved the stable MESH film formations on channels and holes with up to 20 µm-wide openings (Figure 5.10). This process showed the potential capability to integrate thin-film metallic nanostructures with micrometer-scale devices in a simple and high-yield approach, and many novel device applications like drug delivery and liquid cooling will benefit from it.
Figure 5.10 SEM images of 50 nm-thick Au MESH of 130 nm-diameter transferred onto the Si substrate of (a) channels with up to 20 µm width, and (b) 20 µm-width square hole
5.3.4 Transfer printing to flat PDMS substrates

Figure 5.11 35 nm-thick Au MESH transferred on 3 mm-thick PDMS sheet: (a) optical image of a 2 × 2 cm² sample, (b) SEM top view of the transferred MESH
Polydimethylsiloxane (PDMS) is a well-studied Si-containing polymer material for microfluidic device \cite{250-251}, surface electrode \cite{252-253} and OLED \cite{254-255}. It has remarkable advantages such as: (1) optical transparency from 240 nm to 1100 nm with low autofluorescence; (2) bio-compatibility and (3) low cost. However, PDMS is extremely sensitive to process temperature (coefficient of thermal expansion of 310 ppm/ºC) and little resistant to organic solvents, which makes it very difficult to conduct metal coating on PDMS surface with a regular deposition-then-liftoff approach. Transfer printing offers a new pathway to overcome such limitations.

The cured PDMS surface is rich of methyl groups, so it actively shows hydrophobic state with 85º to 93º water contact angle. Still, the PDMS surface chemistry can be easily altered with a brief oxygen plasma treatment to introduce hydrophilic silanol terminations (Si-OH). The more important outcome is the modified PDMS surface can be further functionalized with trichlorosilane-type adhesion promoter to receive patterned Au thin films. 3 nm-thick adhesion promoter (ST-12, Nanonex) was coated on 3 mm-thick PDMS sheet of 2 × 2 cm² area and baked at 110 ºC for 1 min. 35 nm-thick Au was deposited on a 200 nm-pitch h-PDMS flexible mold with 160 nm-diameter holes with E-beam evaporation. A PET mask was placed on top of the mold during evaporation to define Au macro surface electrode patterns. Then the mold was pressed onto the PDMS sheet at 100 Psi and 90 ºC to facilitate the transfer. After cooling down to room temperature, Au electrode arrays with nanoscale holes were transferred and secured on PDMS (Figure 5.11a). The uniform color of Au electrode presented a successful high-yield transfer and was further proved by the detail SEM inspection of Au MESH layer (Figure 5.11b).
5.4 Direct transfer printing of metallic nanostructure by heating

Different from the rigid Si-based substrates, commodity thermal plastics have limited chemical resistance, so they are usually vulnerable to harsh processes with strong organic agents like acetone and xylene. However, these polar solvents are essential parts in typically silane-based surface adhesion promoters as the solvents, making them inappropriate to be applied on the thermal plastics. The flexible natures of thermal plastics also put great difficulties dispensing a uniform coating on a large-area plastic substrate with the typical spin coating method. Therefore, an alternative approach is required to transfer large-area metallic nanostructures to thermal plastic substrates without changing the original mold fabrication and metal deposition procedure.

In such cases, heating up the thermal plastic substrates before the transfer printing can be particularly helpful, because it can weaken the intermolecular forces among the polymer backbone chains, leading to a viscous and moldable state. For any thermal plastic, the glass transition temperature ($T_g$) is a very important property, and is the temperature range where the plastic transitions from a rigid and glassy state into a soft and rubbery state. Heating the plastic to temperatures slightly above $T_g$ will greatly improve its adhesion capability without causing the phase change, so it’s safe to attach the metal coated mold on to the plastic, apply a moderate pressure for conformal contact and then cool down the assembly and peel the mold away, leaving a metallic nanostructure layer embedded on the plastic surface.
Figure 5.12 20 nm-thick Au MESH of 130 nm-diameter transferred onto a transparent 125 μm-thick PET film (a) and it shows great adhesion even when wrapped (b)
To demonstrate this large-area one-step transfer concept, a 125 µm-thick bi-axially oriented, semi-crystalline PET film (DuPont, Melinex®) was selected as the target substrate, and it has a known T_g at 78 ºC. As the most common member of the polyester family, PET is widely used in civilian applications like clothing and food packaging, with advantages in low unit price, high stiffness, great solvent resistance and optical transparency. The PET film was used as received without extra surface cleaning and treatment operations. 20 nm-thick Au MESH was deposited on top of a 200 nm-pitch h-PDMS hole mold by the E-beam evaporation at 1.0 Å/s rate, and brought to contact with the PET film. The assembly was loaded into the nanoimprinter to perform a heating process at 85 ºC, which was slightly higher than the documented T_g. A moderate pressure of 40 Psi was also applied to ensure the conformal contact yet without deeply embedding the nanostructures into the bulk plastic. Finally, the assembly was cooled under a constant nitrogen flow of 25 ºC to solidify the PET film and secure the Au MESH. After the separation, the 1×1 inch² Au MESH was completely transferred to PET (Figure 5.12) with visually uniform optical transmission. The Au MESH was securely bonded to the PET surface, and when the film was wrapped, the Au MESH layer transformed accordingly without cracks and wrinkles.

Based on the same principal, Au MESHs were able to diverse thermal plastic substrates (Table 5.2). The same strategies remain applicable: under a minimal working pressure for large-area contact, heat up the thermal plastic substrates to the corresponding glass transition temperatures.
Table 5.2 Parameters used to transfer 50 nm-thick Au MESH to diverse thermal plastic substrates by heating

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T_g (°C)</th>
<th>Transfer printing parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>100</td>
<td>100 °C, 20 Psi</td>
</tr>
<tr>
<td>PS</td>
<td>90</td>
<td>90 °C, 20 Psi</td>
</tr>
<tr>
<td>PET</td>
<td>78</td>
<td>85 °C, 40 Psi</td>
</tr>
<tr>
<td>PVA</td>
<td>85</td>
<td>90 °C, 10 Psi</td>
</tr>
</tbody>
</table>

Direct transfer printing also enables novel organic electroluminescent (EL) device structures by assemble Au MESH electrode layer onto certain high-performance but delicate organic functional material layers, without harsh chemicals involved.

Bathophenanthroline (BPhen) is a well-known organic material as the electron transport layer in sandwiched EL device architectures [256-257], and it has a relatively high electron mobility (of the order of 10^{-4} \text{ cm}^2/\text{V}) [258]. However, its low glass transition temperature (62 °C) [256] and chemical vulnerability to solvents place strict restrictions to the process that builds transparent MESH electrode layer on top of it. Transfer printing process overcame such restrictions by constructing the MESH layer on a flexible mold and then performing one-step assembling with moderate pressure and temperature close to T_g of BPhen.
Figure 5.13 Direct transfer printing of 160nm-diameter Au MESH to BPhen surface at different temperatures: (a) 30 °C, (b) 60 °C and (c) 90 °C.

80 nm-thick BPhen layer was coated on a p-type Si test wafer, and a direct transfer process attempted to deliver a 20 nm-thick Au MESH layer at 100 Psi and a certain heating temperature. Figure 5.13 presents the transfer results at different temperatures: when the heating temperature was far below $T_g$, BPhen remained in a solid state without sufficient adhesion to trap Au MESH, which resulted in partial transfer (Figure 5.13a); when a heating temperature considerably beyond $T_g$ was applied ($T_g$), the moldable BPhen layer did take over the entire Au MESH layer but viscous BPhen was pushed through MESH vias and spread on MESH top surface (Figure 5.13c), which might deteriorate the device electrical performance; Only when a temperature close to $T_g$ was able to transfer Au MESH with great MESH integrity and flatness without excessive BPhen reflow (Figure 5.13b), and this demonstrated the key role of process temperature in direct transfer printing.
5.5 Summary

A process for large-area high-fidelity flexible mold for transfer printing was developed, featuring modified PDMS polymer with high stiffness and suitable surface energy to support the formation of firm and robust metallic nanostructures on top. The hole mold achieves sub-70 nm resolution features with a 4-inch large area. A thin-layer adhesion promoter approach was design to transfer large-area 50 nm-thick Au MESH structures to rigid Si-rich substrates in a single step of pressing, and its capability was further demonstrated in delivering the entire Au MESH layer onto the top of patterned Si substrates with up to 20 µm gap sizes. By selecting different promotors, Au MESH was able to be sent to the extremely soft PDMS sheets with great integrity and yield. To assemble the MESH structures to promising yet vulnerable thermal plastic substrates, the direct transfer printing method by heating the target substrate to its glass transition temperature was introduced and tested.
Chapter 6

Conclusions

This dissertation has addressed several critical challenges of large-area, high-throughput and cost-efficient nanoimprint lithography (NIL) for (1) generation of complex master mold features, (2) design of novel mold architectures, (3) investigation of high-performance imprinting materials, (4) establishment of alternative nanopatterning techniques based on NIL foundations, and (5) applications of all above in plasmonic sensor fabrication. The combination of these solutions is a complete tool chain to offer robust NIL fabrication.

NIL is a 1:1 high-fidelity pattern replication method, a high-quality master mold with desired nanopatterns is the very foundation of NIL. Many other requirements may apply to achieve better feature controls such as inversion, multiplication and union. By combining LIL and NIL with multi-layer stack, shadow evaporation and double imprint methods (Chapter 2), novel SiO$_2$ master molds with square pillars (135 nm pitch), triangular pillars and moiré patterns in large areas have been successfully generated without the need of complex techniques like DUV photolithography or e-beam lithography.

On the other hand, flexible hybrid polymer mold is a strong trend because it exhibits all-star properties from conformal contact in moderate pressure, extendable large-area capability, simple fabrication procedure, and activated hydrophobic surface without
losing designated resolution performance. A transparent PFPE-based high-fidelity flexible mold (HiF2M) was developed (Chapter 3), featuring fast mold fabrication with UV polymerization, sub-30 nm resolution, area expansion capability (to $50 \times 20 \text{ cm}^2$ and beyond), $> 99\%$ replication fidelity, natural low surface energy surface ($> 97\%$), overlay alignment ability ($< 0.11^\circ$ orientation error) and potential in roller UV NIL fabrication.

The UV-transparent HiF2M mold not only opens a pathway to high-resolution, room-temperature and low-pressure UV NIL, but also brings the motivation to develop high-performance UV NIL resist systems in terms of high-resolution, ideal mechanical and chemical stability, great etching selectivity, low shrinkage and others. Two UV resist systems based on unique POSS monomers are built (Chapter 4): Free-radical system has the highest polymerization rate (typically $< 5 \text{ s}$), improved oxygen inhibition resistance, and close-to-silica refractive index (1.484); Cationic system can be securely cured in the atmosphere with regular grade UV lamps. Both of them possess the common advantages in low shrinkage ($< 6\%$), sub-30 nm resolution, high stiffness, great etching masking to SiO$_2$ and Si, and intact stability in harsh solvents. Using such resists, high-performance plasmonic structures have been fabricated on cost-efficient thermoplastic substrates (PET) and demonstrated in diverse applications from solar cell, OLED to biosensors, to explore the feasibility to replace expensive substrates like fused silica and manufacture devices in a high-through pace.

Besides carrying out UV NIL, flexible polymer mold also enables unconventional nanofabrication technique like transfer printing (Chapter 5) to meet the needs of pattern transfer to promising yet delicate substrates. A modified h-PDMS flexible mold architecture is used to transfer Au-deposited MESH films to rigid Si substrates (up to 20
μm channel width) and soft PDMS sheets with coated adhesion promoting layer. A direct transfer method is also developed for the cases that a thermoplastic target substrate is used with moderate glass transition temperatures. With this metallic nanostructure transfer printing technique, imprinting-based nanopatterning capability is vastly extended to most substrate type without increasing procedure complexity, or compromising feature integrity and uniformity.

It has been the golden age for nanoimprint lithography in the past 20 years with diverse fabrication approaches and application scenarios. Now more and more industrial companies succeed in integrating high-performance photonic components made by NIL into the original designs, and it’s still our duty to further advance the NIL technique into a more reliable and productive state.
Publications

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