ENABLING NANOIMPRINT LITHOGRAPHY TECHNIQUES ACROSS MULTIPLE MANUFACTURING PROCESSES

Vincent Einck
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ENABLING NANOIMPRINT LITHOGRAPHY TECHNIQUES ACROSS MULTIPLE MANUFACTURING PROCESSES

A Dissertation Presented
by
Vincent Einck

Submitted to the Graduate School of
the University of Massachusetts Amherst in partial fulfillment
of the requirement for the degree of

DOCTOR OF PHILOSOPHY

September 2022

Department of Polymer Science and Engineering
Enabling Nanoimprint Lithography Techniques Across Multiple Manufacturing Processes

A Dissertation Presented
by
VINCENT EINCK

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DEDICATION

“When everything seems to be going against you, remember that the plane takes off against the wind, not with it.”

-Henry Ford

Vincent R. Willey
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First, I would like to thank my primary investigator, Professor James J. Watkins. His guidance and mentoring over my Ph.D. journey have been acceleratory to my development as a scientist. Between proposing new ideas and being fully supportive of others, I have been able to gain numerous valuable skills while pursuing a wide variety of research interests. Working with Jim has allowed me to have collaborations and experience with many factions of industry and academia, providing me with an in depth and applied education. His approach to bridging the interface between academia and industry has been one of the greatest skills I look forward to using in my career. Opportunities provided by him or with his help have allowed me to travel and present my research in many forms, to various audiences, providing a valuable skill set for presenting under a breadth of conditions. I have endless gratitude for the opportunities and education he has provided me!

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Advanced nanooptics in the areas of flat lenses, diffractive elements, and tunable emissivity require a route to high throughput manufacturing. Nanooptics are often demanding of high refractive index materials, nanometer precision and ease of fabrication. Nanoimprint lithography (NIL) is a low-cost, high throughput manufacturing technique beginning to be realized in commercial industry.\textsuperscript{1,2} The NIL process is an ideal manufacturing candidate due to its ability to have a fast process time, efficient use of materials, repeatability and high precision while also having wide diversity of potential structures and material choices. Applying NIL techniques to other facets of manufacturing enable the production of a variety of optical structures that require more
strict material or optical properties in combinations of layered materials to provide desired optical contrast or performance.

This Dissertation is designed to study potential new avenues for improving NIL manufacturing through better composite formulation, processing and patterning as well as its applications in final devices. Chapter 1 introduces a variety of fundamental concepts surrounding optical devices, material selection, and applicable advanced techniques for improving NIL techniques. Chapter 1 then emphasizes the applicability of these processes in high throughput manufacturing techniques such as wafer-based manufacturing for rigid substrates and roll-to-roll manufacturing for laminates or flexible substrates. Chapter 2 demonstrates a manufacturable use case for roll-to-roll manufacturing using a seamless drum master, providing a consistent, uninterrupted pattern through the duration of the imprint run.

Chapter 3 introduces composite formulation success using zirconia nanocrystals and a polymeric matrix, providing tunability of the imprint material to target a specific refractive index or match to the substrate of the device. Chapter 4 develops the formulation of titania nanocrystal composites, and their manufacturability into practical metalenses for light collection and focusing. Chapter 5 builds off of the materials developed in chapter 4 with the incorporation of metallized layers for more specific tailorable properties in absorption and reflection. Together, these chapters demonstrate how close NIL is to allowing for the inexpensive, high quality, and low waste manufacturing of a broad range of optical devices for commercial, industrial, aerospace, consumer, and computational markets.
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CHAPTER 1

INTRODUCTION

1.1 Fundamentals of Optics

Optics in isotropic materials is governed primarily by two phenomena: diffraction and absorption. Absorption is a function of the material absorption coefficient and the material thickness. Diffraction is caused by the deceleration of light through a denser media, making it occur strongly at high refractive index mismatch interfaces. Examples include a fish in a stream or a pencil in a glass of water, the refractive index difference between the water and the air makes it appear as though the pencil is bent. Once can imagine that in a glass of even denser water, where the refractive index difference is even higher, that the pencil will look even more bent. Pushing the refractive index of materials for optics is something that has been worked on for decades and has shown advancements in industry already.

1.1.1 Optical Physics

The interaction light has with a media is via its induced dipole, where in dielectric media that match, can absorb that frequency of light, leading to the density and thickness dependence. For materials operating in a regime where the absorption is low, diffraction and reflection dominate. These properties can be used to make lenses, mirrors, beam splitters, waveguides and a variety of other optical devices depending on their angle of usage, refractive indices, and
wavelength of operation. Since diffraction is dependent on the refractive index, increasing the refractive index has the potential for making structures with higher integration density, larger range of diffraction angles, field of view and a shorter focusing distance.

1.1.2 Material selection in optics fabrication using NIL

Current imprinting materials are typically polymeric, or sol gel based. Both have an inherent limitation due to their low optical density and sol gel has the added complication of nanofeature shrinkage and built-in residual stress. These materials are however very easy to work with as their viscosity and solvent content can be maintained over long periods of time due to their low density and flexible molecular characteristics.

A more sophisticated and promising approach is the imprinting of nanoparticle-based materials. Nanocrystals, a form of nanoparticle, have the inherent advantage of having a crystalline core, providing an even higher refractive index than accessible by the amorphous phase as well as a higher structural integrity. Nanoparticle material selection is crucial for the desired application, as ITO nanoparticles can be readily imprinted, but are not transparent in the full visible spectrum. Ideally, a high refractive index, fully visible transparent material would be selected such as TiO$_2$, ZrO$_2$, as well as many others. In addition to material choice, the nanoparticle solution must be comprised of nanoparticles that are less than 1/20th of the wavelength of light in the visible, otherwise they can cause their own scattering. For visible range optics, 400 nm is the shortest desired wavelength, requiring nanoparticles smaller than 20 nm.

Furthermore, a nanoparticle solution must be processable, meaning that they can easily be made into a film. Nanoparticle solutions in water are often charge stabilized or chelated with weak ligands, meaning they become unstable at high concentration or temperature, which are conditions the nanoparticles will experience during spin coating and imprinting. An organic based
nanoparticle solution providing the low surface energy and good dispersibility required for imprinting, often calls for covalently bound or multidentate ligands with surfactants (transiently bound) or ligands (covalently bound).

1.1.3 Optical device designs

Traditional optical devices can be made on the macroscale using lens or prism manufacturing requiring high precision tooling for cutting and polishing curves and edges on glass blanks. For micro and nanooptics, the geometries and precision requirements are up to 9 orders of magnitude smaller. The same optical characteristics of a macroscale optical device can be replicated by flat optic by cutting out the bulk material and making the interfaces act the same by maintaining perceived local curvature on the nanoscale but having no true global curvature.

For the nanoscale equivalent of a prism, instead of having one large prism, you have a surface comprised of pillars with decreasing width as you move along the surface, this enables the diffraction of light, without propagating through the bulk of the prism. A series of these pillars on a surface enable the same behavior of light splaying as you would see in a chronometer, but in much less volume. This is considered a diffractive grating and is very important in the field of virtual reality as it can provide superior peripheral vision without excessive bulk. Additionally, the nanofeature shape and refractive index can be changed to obtain the desired diffraction angle at various wavelengths.

Two-dimensional lenses can use some of the same properties, the diffraction from post arrays can be arranged to converge the light to a single point focusing the input beam just as a bulky curved lens would. Nanofeatures comprised of different pillar widths provide phase delay for individual posts and for assemblies of decreasing pillar width, they form a diffraction grating based on their effective refractive index (larger width, higher effective refractive index).
Concentric circles of these pillars act similarly to a typical lens, instead of the lens thickness providing refraction, a planar film with a gradient effective refractive index focuses the lens by increasing pillar width and phase delay.

### 1.1.4 initiated Chemical Vapor

Initiated chemical vapor deposition (iCVD) is a process by which a thermal radical initiator in the vapor phase is used to initiate free radical polymerization on a surface actively condensing monomer, which is also transported in the vapor phase. Utilizing a controlled vacuum and individual partial pressure of initiator and monomer by adjusting flow rate, very thin films can be deposited.\(^3\)\(^-\)\(^8\) It has been demonstrated that iCVD can be used to make ultrathin battery separators on patterned electrodes. iCVD has also been shown to be effective with the deposition of fluoropolymers, which are often highly desirable due to their nonstick and unreactive properties. Tire manufacturers have started to line molds with fluoropolymer films to facilitate release, which can readily be applied to nanoimprint lithography with careful consideration of film thickness.\(^9\) Additionally, fluoropolymers are known to have a higher oxidation state than carbon dioxide, making them an ideal oxidative barrier for imprinting materials with oxidative reactivity such as metal oxides.

Imprinting metal oxides, specifically in the forms of nanoparticles and nanocrystals, has come to be of interest in the field of optics due to their high refractive index, but often causes deterioration of the PDMS stamp by oxidation of the PDMS network to a silica network by oxidation of the silicon carbon bonds via hydride extraction from a titania or zirconia radical.\(^10\)\(^-\)\(^15\) Titania has been utilized widely for its self-cleaning and UV cleaning properties due to photooxidation.\(^16\)\(^-\)\(^18\) Many specific studies identify the conversion of titania and it’s composites
into higher oxidation states under ultraviolet conditions.\textsuperscript{19,20} As the effects of these varied stimuli lend evidence to material degradation, many researchers have turned to fluorinated or partially fluorinated additives and coatings that facilitate the protection of carbon, metals and metal oxides from oxidation.\textsuperscript{21–24} These fluorinated materials have proven effective as oxidation barrier materials and have pushed the field to investigate fluorinated coatings in depth.

1.1.5 Coatings and colloidal system

Coating systems have a rich history of fascinating development through scalability, improved optical performance, extended durability, and ease of use. The breadth of accessible materials for coating materials is wider than it has ever been and as a result, composites have come to dominate the space.\textsuperscript{25} The key advantage to composites is the ability to tune individual components to achieve the desired optical outcome. Often, composites are comprised of a polymeric or prepolymeric base and a colloidal system to improve absorption and scattering properties. Titanium dioxide is one of the most used materials for coating systems due to its superior durability, and a high refractive index leading to ideal scattering properties. Many formulators have demonstrated work where altering the shape and size of colloidal or patterned components are able to change the scattering and other optical properties such as polarization and absorption.\textsuperscript{26} Additionally, tailoring the orientation, and degree of anisotropy, the effect on optical properties can be observed as well.

Metallized colloidal systems enter a new set of tunable parameters as it increases the reflection at select interfaces and emphasizes any anisotropy in the system depending on the number of metallized facets. Combination of metallization, orientation and dispersion gives an
arsenal of tools for making custom shaped colloids with control over the optical properties over desired facets.

Nanoimprint Lithography (NIL) is a common technique for the fabrication of micro and nanofeatures. Thermal NIL has been shown to be quite effective for a variety of uncrosslinked polymers than conform to the stamp via the use of pressure and heat in excess of the glass transition temperature. Successive demolding realizes the desired structure comprised of the polymeric imprinting material, which could be chosen as an etchable polymer such as poly (methyl methacrylate) (PMMA) or a sacrificial water-soluble release polymer, poly (vinyl alcohol) (PVA). Additionally, the recent development of nanoparticle composite imprint materials has afforded accessibility to the rapid manufacturing of titanium dioxide as well as many other metal oxides in micro and nanopatterning. In combination, this material set, and fabrication process provide a high throughput manufacturing scheme for tailorable shape and size colloidal systems. With a metal evaporation, sputtering and/or electroplating step that can be dropped in place at any point in the fabrication flow, the potential combinations of structure achievable provides a wide range for the broad market of applications.

1.2 High throughput manufacturing processes

In industry, scalability, and manufacturing potential or critical for any project development. Enabling more advanced techniques in already established manufacturing platforms enable seamless transition to higher resolution, more advanced and broader scope of potential designs and devices. This section will illustrate the differences in multiple manufacturing techniques, what their scope and limitations are and why they are designed for their application.
Nanoimprint lithography (NIL) has facilitated a versatile method for producing nanopatterns on a large scale\textsuperscript{34-36}. Since the initial introduction of NIL of thermoplastic materials by heating, by Chou et al., NIL using UV-curable resins (UV-NIL) specifically, has enabled fast production of replicated micro and nanofeatures at ambient temperatures\textsuperscript{37-39}. While both thermal- and UV-NIL can be utilized in the replication of patterns with target applications in semiconductors, photonics, micro and nano-fluidics, sensing, and biological fields, both variations of these processes have traditionally been limited to replication of polymer features, which have refractive indices limited to near 1.5\textsuperscript{40}. As refractive index modulation and control is crucial specifically for optical and photonic applications, such as in displays\textsuperscript{41,42}, anti-reflective LED encapsulants\textsuperscript{43}, and lenses\textsuperscript{44}, new imprint materials are sought that can be used to directly replicate micro and nanopatterns with high index, or index-tunable materials, avoiding the need for typical, subsequent process steps of etching patterned polymers and depositing high-index materials.

Several different approaches to increasing the refractive index of polymers have been reported. For example, much work has focused on the synthetic design of high refractive index polymers, which involves incorporating substituents with high atomic refractions such as aromatic rings and halogen and sulfur atoms. For example, refractive index modulation from 1.68 to 1.79 has been demonstrated by varying the sulfur and aromatic content of polyimides\textsuperscript{45,46}. Though a high index can be achieved using this method, and with conjugated polymers the index reaches up to 2.7, these polymers often suffer from low solubility, high optical dispersion, and low optical transparency, making them poor candidates for many optical applications\textsuperscript{47}. Another approach involves adding high refractive index, inorganic nanoparticles within a polymer matrix. High index materials such as crystalline TiO\textsubscript{2}, ZrO\textsubscript{2}, and amorphous silicon are commonly used, as they are transparent in the visible region. Nanoparticles must be smaller than 40 nm and well-dispersed
throughout the matrix to maintain optical transparency\textsuperscript{48,49}. In 2014, Beaulieu et al. demonstrated nanoimprinting of a TiO\textsubscript{2} nanoparticle/UV-resin composite where control over refractive index was achieved from 1.58 to 1.91 (\(\lambda=800\) nm)\textsuperscript{50}. This approach, however, requires the use of significant quantities of volatile solvents. In addition, the use of TiO\textsubscript{2} in polymer composites, particularly for light-based applications, raises concerns about degradation resulting from the photocatalytic properties of TiO\textsubscript{2}.

\textbf{1.2.1 Wafer based manufacturing}

Wafer based manufacturing is required for manufacturing of inherently brittle materials such as all inorganics. Inorganic materials have a very small strain to break, making them highly inelastic, meaning that any type of bend or stretch in the substrate will cause fracture of the inorganic layer. Therefore, a rigid substrate such as silicon, sapphire, high refractive index glass, borosilicate glasses, fused silica or many others can support an all-inorganic film. The substrate selection dictates the device design and material selection as the film to substrate interface influences the optical performance, sometimes requiring refractive index matching to negate any optical effects at the interface. For some applications, designing the film to substrate interface can be advantageous and therefore a low refractive index substrate can be used.

Wafer based manufacturing for NIL consists of an automated tool that can clean, coat, imprint, cure and release a whole cassette of substrates. A cassette of blank wafers and imprint material can be loaded into the tool, and it will actuate an arm to obtain a wafer and transfer the wafer to the spin coater. The spin coater can then clean the substrate with solvent and deposit a film of low viscosity imprint material. The arm is actuated again to transfer the coated wafer to the imprint section. The imprint section uses a series of pneumatically actuated cavities that expand to
depress a glass backed stamp onto the uncured imprint material, which fills the stamp features by capillary action. After full contact is made, UV exposure provides the solidification for the feature fabrication and subsequent release of the stamp via the pneumatic tool. The arm actuates again to transfer the imprinted substrate into the completed cassette and then begins the process again.

Flat optics are of ever-increasing interest due to their space and weight efficiency. A traditional lens uses its curvature and resulting thickness to refract light, where a flat lens can achieve the same level of diffraction in multiple orders of magnitude less in thickness (500 nm compared to 500 μm) and a fraction of the weight.\textsuperscript{51–54} In addition to size and weight efficiency, two dimensional lenses fabricated by NIL require minimal material and tool costs due to the small amount of imprint material required for additive manufacturing. Power consumption is utilized efficiently by localizing the energy to the active layer by using a specific wavelength selected for the imprint material. Fundamental advantages in each of these categories shows promise for NIL to be the most efficient process for manufacturing metasurfaces at a commercial scale with some SWaP-C optimization. Overcoming the hurdles of mass production of these lenses is a primary barrier to entry into commercial, defense, fiber optic transmission and consumer markets. Given a reliable manufacturing process for these two-dimensional lenses, their replacement in many optical applications becomes feasible. Due to NIL having high precision over the manufacturing and pattern replication of nanofeatures, better control over lens design and resulting performance provide the ability to tune the lenses to the optimal structure over device generation improvements.

In a world of ever progressing semiconductor technology, where defect limits are sub ppm and resolution is ever progressing toward atomic, NIL is often overlooked.\textsuperscript{55} In the field of optics, defect limits can be accounted for and tolerated beyond the requirements for semiconductor manufacturing.\textsuperscript{56} Due to averaged performance, resolution is only required to be within 10 nm
making NIL is a superior tool due to its ease and low cost, making accessible to more researchers and manufacturers. In a single step of NIL, structures requiring 3 to 5 steps by patterning and etch can be fabricated in under 2 minutes total process time. Multistep processes generally require patterning and etching tools to provide the desired features, which take hours of operation and at high expense in terms of energy, labor, and materials. Etch based processing also requires a large-scale patterning system limiting it to deep UV, due to the excessive cost of e-beam patterning on a large scale. With NIL, a single Deep UV patterned master can be used to make a countless number of stamps, which can then be used to make 10-100 imprints each, making the scalability drastically improved.

NIL has been shown to have nanometer resolution in a broad range of materials from pure polymers, prepolymer, sol gel, and composites. Recent publications have showed improved performance from composites over sol gel as shrinkage in the fabricated structure is 10% with nanoparticle-based formulations and up to 90% for many sol gel systems. For optics, composites show promise over pure polymers as their ceiling for refractive index is much higher. Generally, inorganic materials have a significantly higher refractive index compared to polymers due to their atomic and resulting optical density difference. By choosing optically transparent, high refractive index materials, polymer based optical resins can have a refractive index boost by loading with zirconia nanoparticles. Titania, however, is a photooxidation catalyst and therefore oxidizes the polymeric matrix over an extended UV exposure leading to yellowing over time. The photooxidation of titania can also be used as a catalyst for air scrubbing, self-cleaning windows, antimicrobial wands, and may other applications. Herein, we present a method for utilizing the photocatalytic ability of titania to cure a nearly pure inorganic structure for the application of flat optics, replacing polymer composites with high thermal tolerance inorganics.
1.2.2 Roll-to-roll manufacturing

Roll-to-roll manufacturing is the ideal case for manufacturing nanopatterns that can tolerate a flexible substrate. For imprint resins of this type, fully inorganic structures cannot provide the desired curvature without fracture, therefore a polymeric matrix must be included to allow for flexibility. Loading a high refractive index prepolymer with high refractive index crystalline nanoparticles allows for a flexible and patternable material with high refractive index. An added benefit of this system is the ease of manufacturing due to the fluidity provided by the prepolymer matrix. While the maximum achievable refractive index is lower due to the incorporation of polymer, the range of achievable structures and potential substrates is much more applicable to broader market.

Roll-to-roll manufacturing has a history embedded in the paper industry and therefore coating and patterning processes have already been highly researched and established. Additionally, the scalability of the process has already been proven for printmaking, but further advancement in NIL materials may enable the technology to break into the consumer optics sector and reutilize machinery that is doomed to run idle. By using the same coating techniques but developing an imprinting module and material for imprinting could afford a scalable approach to making any number of optical devices on laminate substrates that can then be applied directly to consumer optics or other packaging applications.
CHAPTER 2
NANOIMPRINT LITHOGRAPHY USING A SEAMLESS CYLINDRICAL MOLD
NANOPATTERNED WITH A HIGH-SPEED ROLL-TO-ROLL MASTERING PROCESS

2.1 Introduction

Roll-to-roll (R2R) processing has enabled large-area, low-cost manufacturing of products ranging from packaging to printed electronics. R2R nanoimprint lithography (NIL) seeks to apply high-throughput R2R techniques to nanopattern films for high-tech applications such as displays, augmented and virtual reality, and antimicrobial or self-cleaning surfaces. R2R NIL uses a cylindrical mold to continuously imprint a nanopattern into a film as illustrated in Figure 2.1. Despite its potential, R2R UV NIL has thus far been limited by the infeasibility of nanopatterning large-area seamless cylindrical molds, which is prohibitively time consuming and expensive with traditional lithographic techniques. Smart Material Solutions, Inc. overcomes this bottleneck with its high-speed nanopatterning process, nanocoining, which can nanopattern cylindrical molds hundreds of times faster than electron-beam lithography. This chapter presents the seamless patterning of a 6.5” diameter mold with 600 nm and 2 µm features using the nanocoining process and the use of this mold on a through substrate UV R2R NIL setup to nanopattern more than 60 linear feet of polymer film.
Nanocoining offers several advantages over traditional lithographic techniques including its high speed, seamless patterning, and control of 3D feature shape. Traditionally, cylindrical nanopatterned molds are created by wrapping a planar, flexible, patterned shim around a cylindrical drum, leaving behind a seam where the edges meet, which can cause manufacturing difficulties through increased adhesion and is undesirable for many applications, like television displays. Nanocoining is a high-speed indenting process that seamlessly patterns around the outside of a cylinder hundreds of times faster than electron-beam lithography. Seamless patterning of cylindrical molds has also been demonstrated with interference lithography and electron-beam lithography, but unlike nanocoining, these approaches can require weeks or more to create a single large-area mold and are often limited to larger feature sizes. Nanocoining also offers 3D control of feature shape, which can dramatically affect the optical and wetting properties, whereas traditional photolithography produces binary features that can be rounded with imprecise processes like resist reflow or etching. Nanocoining’s exceptionally high speed makes it unique in its ability to create a one-square-meter seamless drum mold with engineered 3D feature shapes in less than one day of continuous patterning. This chapter presents a proof-of-concept study demonstrating the promise of nanocoining for the creation of seamless nanopatterned cylindrical molds for UV NIL R2R manufacturing through the substrate.
2.2 Experimental Section

2.2.1 Fabrication of seamless cylindrical mold

Figure 13.2 shows a photo of the cylindrical metal mold used to pattern 60 linear feet of film using through substrate UV R2R NIL. The highly scalable nanocoining process, discussed below, was used to seamlessly pattern the outside of this 6.5” diameter by 6” long tube with strips of 600 nm features (top) and 2 µm features (bottom). The mold consists of an aluminum tube coated with a high-phosphorous nickel coating (NiCoForm, Inc. Rochester, NY) with a hardness of 48 Rockwell C, which is comparable to the hardness of hardened 420 stainless steel.\textsuperscript{74,75} The mold was patterned by creating more than 2.8 billion indents in about two hours (Table 2).

![Photo of the 6.5” diameter master mold used throughout this chapter.](image)

**Table 2**

<table>
<thead>
<tr>
<th>Feature</th>
<th>Description</th>
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</thead>
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<td>600 nm</td>
<td>Micron-sized features</td>
</tr>
<tr>
<td>2 µm</td>
<td>Larger micron-sized features</td>
</tr>
</tbody>
</table>

**Figure 13.2** Photo of the 6.5” diameter master mold used throughout this chapter.
Table 2.1 Metrics for indenting of 6.5” diameter master mold.

<table>
<thead>
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<tbody>
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<td>0.6</td>
<td>39</td>
<td>1.1 billion</td>
<td>69.9 billion</td>
<td>50</td>
<td>0.78</td>
</tr>
<tr>
<td>2.0</td>
<td>65</td>
<td>1.7 billion</td>
<td>10.5 billion</td>
<td>79</td>
<td>0.83</td>
</tr>
</tbody>
</table>

2.2.2 Nanocoining Process Overview

Nanocoining is a high-speed nanopatterning technique that uses a patterned diamond die (Figure 2.14) to mechanically indent the outside of a metal drum mold. In the first step, a focused ion beam (FIB) patterns the tip of a diamond over an area of about 200 µm². Single-crystal (100) diamond shanks (Chardon Tool & Supply, Chardon, OH) were patterned using a FEI Quanta 3D DualBeam SEM/FIB at the North Carolina State University (NCSU) Analytical Instrumentation Facility (AIF).

Figure 2.14 Photo of a diamond die with SEM of feature patterned in its tip. The first step of the nanocoining process is the nanopatterning of the tip of a diamond die using FIB milling.
The nanopatterned diamond die is then mounted on a custom-made ultrasonic resonant actuator that vibrates along an elliptical path at 45,000 Hz. The vibrating die is brought into contact with a rotating metal workpiece such that the diamond indents the workpiece once per ellipse, replicating the diamond’s nanopattern into the metal surface with each indent (Figure 2.15). The diamond’s elliptical path ensures that the surface speed of the diamond matches that of the rotating metal workpiece during the 1-2 µs of contact for each of the 45,000 indents created every second. This process creates a seamless spiral of indents around the outside of the cylinder and enables coverage rates up to about 2 in²/min – hundreds of times faster than traditional processes like electron-beam lithography.62,63

Figure 2.15 Illustration of the nanocoining indenting process during which a diamond die indents a metal cylinder 45,000 times per second.

The motion of the cylindrical master mold and ultrasonic actuator are controlled with a custom-built, high-precision CNC lathe that consists of an air-bearing spindle (Professional Instruments Co., Hopkins, MN) and a set of orthogonal X-Z linear stages (Aerotech, Inc. Pittsburgh, PA) mounted on a repurposed coordinate measurement machine (Figure 2.16). This system diamond turns the metal to ~10 nm RMS surface finish prior to indenting. During indenting, the spindle rotation speed, ellipse shape, actuator frequency, and X-Z axis positions are precisely controlled to enable side-by-side tiling of indents and to prevent smearing.
2.2.3 Roll to roll UV Nanoimprint Lithography

The 6.5” cylindrical mold was used to fabricate 60 linear feet of patterned polymer on the through substrate R2R UV NIL setup at the University of Massachusetts at Amherst (UMass - Amherst). This setup, shown in Figure 2.17, uses a UV lamp to cure a proprietary photopolymer from Sun Chemical on a PET film (Tekra MELINEX® ST505 ) while it is in contact with the cylindrical mold. The NanoEmboss 100 platform from Carpe Diem Technologies allows for UV illumination through the transparent PET film to cure the photopolymer while it is in contact with the non-transparent nanocoined nickel drum. This platform enables tension control of the
PET web as it goes through unwind, coating, drum contact, cure, release, and rewind. Coating of the photopolymer was conducted with a Meyer rod at a line speed of 20 in/min.

Two photopolymers were tested using the same R2R platform: Norland Optical Adhesive 65 (NOA65) and Sun Chemical high refractive index photopolymer. NOA65 utilizes thiolene click chemistry and the Sun Chemical photopolymer is an acrylate-based formulation. It was found that thiolene photopolymers show increased adhesion to the nickel drum, likely due to the strong metal-thiol bond. The acrylate system showed low adhesion to the drum due to the absence of thiol functionalities. For these imprint trials, a film thickness greater than the feature height is used to ensure feature filling, but depending on the nanofeature geometry and uniformity, voids or hole features can trap bubbles and prevent filling. Additionally, sharp edges can be encased by the photopolymer, removing individual features due to adhesion on localized high surface areas burs. Recessed volumes allow for the polymer to fill, but upon curing the undercutting of the recesses prevent the structure from being able to release without breaking, resulting in the embedding of the photopolymer into the features of the nanocoined drum.

Figure 2.17 Photos of the patterned mold on the through substate (not in photo) R2R UV NIL at the University of Massachusetts at Amherst.
2.2.4 Metrology

Scanning electron microscopy (SEM) was performed with a FEI Quanta DualBeam FIB/SEM to examine the diamond dies and metal mold. The diamond was imaged with the SEM immediately after the completion of the FIB milling process since the instrument has both an SEM and FIB. The 6.5” metal mold was too large to fit into the SEM, so the mold was cut into smaller 2x2” pieces for SEM examination after the R2R processing was completed. SEM of the patterned polymer films was performed on a FEI Magellan 400 XHR-SEM and a FEI Quanta DualBeam FIB/SEM. The nanopatterned polymer films were coated with ~10 nm of a gold-palladium alloy prior to their examination in the SEM to prevent charging. Small scale nanopatterned polymer films were also created using batch processing by curing Norland Optical Adhesive 65 (NOA65) on a polycarbonate backing (Tekra 8010) while in contact with an indented metal mold. After curing, the films were peeled off the molds and examined using an Asylum MFP-3D atomic force microscope (AFM) in tapping mode with Opus 240AC-NA tips.

2.3 Results and Discussion

Figure 2.18 show SEM images of the diamond die, indented metal mold, and R2R-imprinted polymer film for the features with a pitch of 2 µm. The diamond dies show good uniformity with all features appearing roughly the same shape and size. There is no visible seam between the separate indents making up the micropatterned regions because of the well aligned diamond die and proper matching of the tangential speeds of the diamond and the rotating metal cylinder during the indenting process. Buildup of metal around each indent as a result of material flow during indenting is apparent in the SEM images of the metal mold and R2R-replicated polymer film and the AFM images of the batch-processed polymer films shown in Figure 2.19.
Figure 2.18 SEM images of 2 µm features in the diamond die (top), indented metal mold (middle), and R2R-replicated polymer film (bottom).
Figure 2.19 AFM images of 2 µm features in NOA 65 polymer film replicated using batch replication processes at 80 µm by 80 µm (left) and 8 µm by 8 µm (right).

One defect observed in some regions of the indented 2 µm features is the repeated absence of a feature due to a feature breaking off the diamond die, causing the resulting void to be replicated in every indent afterwards. Breaking of the diamond die’s features may be due to a hard particle in the cylinder’s metal coating, contamination, or shearing of features due to poor tangential speed matching between the diamond die and the metal surface during indenting. Tall, high aspect ratio features may be particularly susceptible to breaking.

Figure 2.20A shows an optical microscopy image of the metal mold with a red arrow pointing to the one indent out of the mold’s 1.7 billion indents that caused features to break from the diamond die. The SEM images in Figure 2.20B and Figure 2.20C show the repeated void that results from indenting with a diamond with missing features. These voids can be filled as shown in Figure 2.20D by indenting each part of the metal mold multiple times with different parts of the diamond die. This correction process can be achieved by adjusting the cylinder rotation speed and/or the axis cross feed speed during indenting such that each region is indented more than once. Other methods to reduce this error include using lubricants and engineered material coatings to prevent the breaking of diamond features.
Figure 2.20 An optical microscopy image of mold with 2 µm features with a red arrow indicating the indent at which a feature breaks off of the diamond die (A) and SEM images a polymer film showing the resulting repeated voids (B,C) and the elimination of these voids by double indenting.

SEM images of the 600 nm features in the diamond die, indented metal mold, and R2R-imprinted polymer film are shown in Figure 2.21. Imperfect speed matching of the diamond die and rotating metal drum during indenting results in some smearing of the features that is particularly apparent in the close-up SEM images of the metal mold and polymer film. In
addition, some misalignment of the diamond die’s roll angle results in the indents not perfectly tiled together, resulting in a seam that is visible between each indent in the microscopy images.

![Diamond Die](image1)

![Metal Mold](image2)

![Polymer Film](image3)

**Figure 2.21** SEM images of 600 nm features in the diamond die, indented metal mold, and through stamp UV NIL R2R-replicated polymer film.
Both the metal mold and polymer film also exhibit some missing features. The missing features in the metal mold repeat in every indent, indicating that these missing features are due to features missing from the diamond die, as was the case for the previously discussed 2 µm features.

While some features missing from the polymer film are repeated in every indent, other features are missing from some indents and present in others, suggesting that some of the missing polymer features are a result of the imprinting process from this master. Possible explanations could be incomplete filling of the metal mold with the uncured polymer due to trapped voids, clogging of the metal mold with another material prior to its use in the R2R setup, or embedded polymer features as the polymer film is released from the cylinder after curing. It is possible that the smaller size of the 600 nm features makes them more fragile and thus more susceptible to these problems than the 2 µm features. More experiments are needed to identify the cause of these nonperiodic missing features. It is worth noting that AFM (Figure 2.22) and SEM (Figure 2.23) of NOA65 polymer films made with batch-processing techniques do not exhibit these nonperiodic missing features, indicating that the nonperiodic missing features are likely a result of the specific R2R processing conditions and not polymer replication in general.

**Figure 2.22** AFM images of 600 nm features in NOA 65 polymer replicated using batch replication processes.
Figure 2.23 SEM images of 600 nm features in NOA 65 polymer film replicated using batch-replication processes showing the absence of nonperiodic missing features.

The 3D shape of nanofeatures can have a big effect on their optical and wetting properties.\textsuperscript{68,69} It is therefore important to understand how the shape and size of the features evolve between the diamond die, indented metal mold, and replicated polymer film. Figure 2.24 shows side-angle SEM images used to estimate and compare the cross-sectional profiles of features in the diamond dies and R2R-replicated polymer films. All images were taken with a tilt angle of 75°, and trigonometry was used to correct for the tilt angle. Note that this method can result in a small error, since it extracts the profile from a point just beyond the top of the feature rather than from the exact top of the feature. The extracted cross-sectional profiles are shown in Figure 2.25. For both the 600 nm and 2 µm features, cross sections of three features from the diamond (shades of blue) are shown alongside the cross sections of three features from the R2R-
replicated polymer film (shades of orange). The shape and size of the diamond features are very consistent for both feature sizes; there is more variability between features in the replicated polymer films, which is likely due to variability in the mold-indenting, polymer filling and replication processes.

**Figure 2.24** Side-angle SEM images of the 600 nm and 2 µm features in diamond and R2R-replicated polymer replicas. All images are taken with a tilt angle of 75°.
A) 600 nm features

B) 2 µm features

Figure 2.25 Cross-sectional profiles extracted from the side-angle SEM images in Figure 2.24. Each plot shows three features from the diamond and three features from the R2R-replicated polymer in shades of blue and orange, respectively.

In some cases, the widths of the features are larger in the polymer films than in the diamond dies. This is likely due to some smearing of the features due to a mismatch between the tangential speeds of the diamond die and the metal mold during the mold-indenting process. This smearing is more severe for the 600 nm features than for the 2 µm, as is also evident from the SEM images in Figure 2.20 and Figure 2.21.

For both feature sizes, the feature heights in the diamond die are larger than the heights observed in the polymer films. The features with a pitch of 600 nm exhibit heights of ~250 nm.
and ~215 nm in the diamond and the polymer film, respectively. The height of the 2-µm-pitch features decreases from ~1100 nm in the diamond to only ~550 nm in the polymer film. This change in feature height is due to a combination of factors. First, if the diamond die does not bottom out during indenting, only the tops of the features will indent the metal mold, resulting in shorter features in the metal than in the diamond. In addition, the metal mold will experience a combination of plastic and elastic deformation during indenting, and only the plastic deformation will result in a permanent indent. Upon removal of the diamond die each indent, the metal will experience elastic spring back which result in shorter features in the metal mold. Finally, the polymer can incompletely fill the mold, resulting in replicated polymer features sizes that are smaller than the features in the metal mold. It is therefore not surprising that the diamond feature sizes are taller than the features in the replicated polymer films.

2.4 Conclusions and future work

This chapter presents the rapid, seamless nanopatterning of a cylindrical mold using a novel, scalable processes known as nanocoining and the use of this mold to pattern more than 60 linear feet of polymer film on a roll-to-roll (R2R) nanoimprint lithography (NIL) setup. This method enables extremely fast patterning of large areas with two nanopattern-multiplication steps. First, nanocoining uses a vibrating, nanopatterned diamond die to indent a metal mold, creating 45,000 copies of the diamond’s nanopattern every second. The resulting metal mold is the used in a through substrate R2R UV NIL setup to rapidly copy the mold’s pattern into a polymer resin on PET. SEM and AFM are used to examine and compare the features in the diamond die, metal mold, and polymer film. By combining the scalability of nanocoining, R2R processing, and UV NIL, this method enables the scalable manufacturing of large-area, low-cost
nanopatterns for advanced technologies relying on metamaterials, plasmonic structures, and nanopatterned surfaces.
CHAPTER 3

Solvent-Free, Transparent, High-Refractive Index ZrO₂ Nanoparticle Composite Resin for Scalable Roll to Roll UV-Nanoimprint Lithography

3.1 Introduction

Nanoimprint lithography (NIL) has facilitated a versatile method for producing nanopatterns on a large scale. Since the initial introduction of NIL of thermoplastic materials by heating, by Chou et al., NIL using UV-curable resins (UV-NIL) specifically, has enabled fast production of replicated micro- and nanofeatures at ambient temperatures. While both thermal- and UV-NIL can be utilized in the replication of patterns with target applications in semiconductors, photonics, micro- and nano-fluidics, sensing, and biological fields, both variations of these processes have traditionally been limited to replication of polymer features, which have refractive indices limited to near 1.5. As refractive index modulation and control is crucial specifically for optical and photonic applications, such as in displays, anti-reflective LED encapsulants, and lenses, new imprint materials are sought that can be used to directly replicate micro- and nanopatterns with high index, or index-tunable materials, avoiding the need for typical, subsequent process steps of etching patterned polymers and depositing high-index materials.

Several different approaches to increasing the refractive index of polymers have been reported. For example, much work has focused on the synthetic design of high refractive index polymers, which involves incorporating substituents with high atomic refractions such as aromatic rings and halogen and sulfur atoms. For example, refractive index modulation from 1.68 to 1.79 has been demonstrated by varying the sulfur and aromatic content of polyimides. Though a
high index can be achieved using this method, and with conjugated polymers the index reaches up to 2.7, these polymers often suffer from low solubility, high optical dispersion, and low optical transparency, making them poor candidates for many optical applications\textsuperscript{47}. Another approach involves adding high refractive index, inorganic nanoparticles within a polymer matrix. High index materials such as crystalline TiO\textsubscript{2}, ZrO\textsubscript{2}, and amorphous silicon are commonly used, as they are transparent in the visible region. Nanoparticles must be smaller than 40 nm and well-dispersed throughout the matrix to maintain optical transparency and avoid losses in optical performance to scattering from soft aggregates\textsuperscript{48,49}. In 2014, Beaulieu et al. demonstrated nanoimprinting of a TiO\textsubscript{2} nanoparticle/UV-resin composite where control over refractive index was achieved from 1.58 to 1.91 ($\lambda$=800 nm)\textsuperscript{50}. This approach, however, requires the use of significant quantities of volatile solvents. In addition, the use of TiO\textsubscript{2} in polymer composites, particularly for light-based applications, raises concerns about degradation resulting from the photocatalytic properties of TiO\textsubscript{2}. ZrO\textsubscript{2} composites are advantageous to their TiO\textsubscript{2} counterparts due to the higher band gap of ZrO\textsubscript{2} and significantly decreased photocatalytic activity, raising fewer concerns about polymer matrix oxidation resulting in polymer chain scission.\textsuperscript{76–78} This fundamental limitation of the polymeric based titanium dioxide composite systems can be remedied by using a high refractive index nanoparticle with significantly less photooxidation activity such as zirconium dioxide.

In this work we combine two methods in order to increase the refractive index of UV-curable monomers: the addition of ZrO\textsubscript{2} nanoparticles to an acrylic UV-curing monomer, as well as to a mixture of UV-curable monomer and the high refractive index small molecule, N-vinylcarbazole (NVC). The resulting material is UV-curable and solvent-free, making it an attractive resin for scaling to large scale production, including roll-to-roll manufacturing.\textsuperscript{79}
3.2 Experimental Section

3.2.1 Fabrication of Zirconia composites

Monomer Miramer 1142 (M1142) was provided by Miwon Specialty Chemical Co. Ltd. A 6 nm Zirconium Dioxide (ZrO$_2$) nanoparticle dispersion (50 wt% in propylene glycol monomethyl ether acetate) was purchased from Pixelligent Technologies LLC. The photoinitiator Esacure KL200 was provided by Lamberti. Propylene glycol monomethyl ether Acetate (PGMEA) and N-vinylcarbazole (NVC) were purchased from Sigma Aldrich. All materials were used without further purification. M1142 and ZrO$_2$ composites were prepared by mixing the liquid monomer with the nanoparticle dispersion in varying concentrations. Mixtures of M1142 with 0 to 30 vol% ZrO$_2$ were prepared (with respect to total solids). Mixtures were prepared in glass dishes, placed on a magnetic stir/hot plate at 65°C, and left overnight. Mass loss was monitored to ensure the removal of all PGMEA from the ZrO$_2$ dispersion. M1142/NVC composites were prepared by mixing solid NVC with M1142 monomer in various ratios in glass vials, which were then stirred and heated above the melting point of NVC (65°C) until the NVC was melted and dissolved into the M1142 monomer. These M1142/NVC mixtures were then used to prepare M1142/NVC/ZrO$_2$ composites the same way the M1142/ZrO$_2$ composites were prepared. 3% of KL200 photoinitiator was added after solvent removal.

3.2.2 Preparation of smooth and nanopatterned films

Composite mixtures were pipetted onto an anti-adhesion treated silicon stamp and covered with a piece of Melinex ST505 PET (poly(ethylene terephthalate)) film. A roller was used to evenly spread the resin, and the resins were then cured under 1 mW/cm$^2$ 365 nm UV light for about one minute. Thin films (< 500 nm) were prepared for ellipsometry measurements by diluting the
different composite mixtures with PGMEA to 10 wt% (with respect to all solids). These solutions were then spin coated onto silicon wafers and cured under nitrogen. 150 µm films for UV-Vis spectroscopy were prepared by pressing resin between two glass slides separated by a 150 µm cover slip. Both glass slides were treated with an anti-adhesion layer for easy removal after curing.

3.2.3 Roll to roll processing

The stamps for roll-to-roll imprinting were prepared using Sylgard 184, a 2-part silicone elastomer that was mixed at a 10:1 ratio and degassed under vacuum. The degassed silicone mixture was spin coated onto an anti-adhesion treated silicon master at 2000 rpm. The silicon master and the liquid silicone were then put into a 75ºC oven for 4 hours to complete the thermal cure. The stamp was then returned to the spin coater and another layer of Sylgard 184 was spin coated at 2000 rpm and a 3-mil polyester silicone release liner (MPI Release Liner 142 GA PET) was placed on the spin-coated, liquid-silicone side. The entire construction was placed in an oven for 24 hours at 75ºC. Afterwards, the PDMS replica and release liner were peeled off the silicon master.

UV-assisted roll-to-roll nanoimprinting was conducted using a R2R Nano Emboss 200, which was custom designed and manufactured by Carpe Diem Technologies. The PDMS stamp, release liner assembly was wrapped on the six-inch diameter quartz drum (15.24 cm) encasing a 365 nm UV LED lamp in order to enable through stamp illumination. A mixture of 70 vol% M1142, 30 vol% ZrO₂ and 3 wt% photoinitiator was prepared and was coated using a Meyer rod. Optical grade 125 µm PET film was used as the substrate and cleaned by a 5-Watt corona treatment before coating. 365 nm wavelength UV light at a 5 Watt/in² (0.775 Watt/cm²) power density (irradiance) was applied for cure. The R2R imprinting line was run at 30 in/min (76.2 cm/min). The cured
imprinted pattern is shown in Figure 3.1a. as it emerges from the imprinting station and in Figure 3.1b. as it enters the rewind station.

![Image of imprinting process](image)

**Figure 3.1** R2R imprinting of the M1142/20 vol% ZrO$_2$ resin on PET. a. image of the patterns emerging from the imprint station and b. image of the patterns imprinted on PET just prior to the rewind station.

### 3.2.4 Characterization methods

The refractive index ($n_D$) at $\lambda = 589$ nm (sodium D-line) of uncured composite resins were measured using an ATAGO NAR-1T refractometer. Films were cured using 365 nm UV light with ca. 1 mW/cm$^2$ from a biostep® USDT-20ML-8R source. Imprinted patterns were imaged using an Olympus BX51 optical microscope. UV-Vis spectra were obtained using a Perkin Elmer Lambda 900 UV/VIS/NIR-spectrometer. The refractive index of cured films was obtained using a JA Woollam RC2 variable angle spectroscopic ellipsometer. Ellipsometric data from 55-75° was fit using the Cauchy model in the CompleteEase software. Height profiles of patterned films were obtained using a Zygo Nexview Optical Profiler.
3.3 Results and Discussion

Miramer 1142 (M1142) is a commercially available acrylate monomer with a relatively high refractive index ($n_D=1.58$), and was therefore chosen as the matrix/base component of our high index composites. The high refractive index of M1142 (figure 3.2a) arises from its chemical structure, which possesses aromatic rings such as biphenyl (M1142). In order to further increase the matrix refractive index, we also selected the N-vinylcarbazole (NVC) shown in Figure 3.2b as an added co-monomer to the already commercially available M1142. NVC exhibits a refractive index of $n_D= 1.68$.

![Chemical structure of a) M1142 (o-phenylphenol ethyl acrylate) and b) N-vinylcarbazole.](image)

Figure 3.2 Chemical structure of a) M1142 (o-phenylphenol ethyl acrylate) and b) N-vinylcarbazole.

Zirconium dioxide (ZrO$_2$) nanoparticles (NPs) were added to and dispersed in M1142 in order to further increase the refractive index. After adding the ZrO$_2$ NPs (up to 30 vol% with respect to total solids) and removing the solvent, the composite resins maintained their
transparency and no aggregation was visible by visual inspection. This indicates a good dispersion, which is a result of the compatibility of the ZrO$_2$ capping agents and M1142. Further indication of a good dispersion is evident in the linear increase in refractive index as vol% of ZrO$_2$ increases, as shown in Figure 3.3a. Due to the NPs’ small size (6 nm) and good dispersion within M1142, the composite acts as an optically homogeneous material with negligible light scattering contributions from the NPs at visible wavelengths. The refractive index of the uncured M1142/ZrO$_2$ composites can be tuned from 1.58 to just under 1.69 by adjusting ZrO$_2$ vol% from 0 to about 30%.

**Figure 3.3** Refractive index $n_D$ of M1142 with increasing ZrO$_2$ loading (a), and refractive index $n_D$ of M1142/NVC composites. Both measured before curing with 3% photoinitiator added.

To obtain even higher refractive index composites, NVC was added to M1142 to create a higher index starting matrix material for the ZrO$_2$ composites. NVC is a solid at room temperature with a melting point at 66°C, and is therefore not easily imprinted. However, we were able to pattern NVC by heating a glass slide and then quickly curing, as shown in Figure 3.4. Mixtures of M1142/NVC were prepared in weight ratios from 1/1 to 4/1. As NVC concentration increases, so does the refractive index, as shown in Figure 3.3b. Mixtures with NVC weight ratios greater than
M1142/NVC 1/1 resulted in a semi-solid material, non-transparent material unsuitable for preparing composites. Adding NVC to M1142 can increase the matrix refractive index from 1.58 to 1.64, while also maintaining a transparent, and imprintable liquid resin.

Figure 3.4 Manual imprints of NVC on glass including cross, grid and hole structures. Scale bar is 20 µm.

Composites containing ZrO$_2$ loadings between 0 and 30 vol% were prepared using the M1142/NVC matrix mixtures. As shown in Figure 3.5a, the refractive index of the starting material is increased due to addition of NVC. As the concentration of ZrO$_2$ increases, the refractive index is also increased, and we note that for M1142/NVC = 2/1 with 30 vol% ZrO$_2$, we can achieve an index above 1.7 for uncured composites. We do note that though the M1142/NVC = 1/1 mixture has the highest starting index, at 30 vol% ZrO$_2$ loading, the index is less than that of the 30 vol% M1142/NVC 2/1 sample. This result is due to agglomeration of the nanoparticles, which is confirmed by the milky appearance of the 30 vol% ZrO$_2$ M1142/NVC 1/1 composite resin. As higher concentrations of NVC are added, the mixture viscosity increases, which may inhibit the
dispersibility of the NPs. The M1142/NVC = 1/1 mixture with 30 vol% ZrO$_2$ has an approximately equal refractive index value with M1142/NVC = 4/1 and 8/3.2.5 with 30 vol% ZrO$_2$. Mixtures of M1142/NVC = 4/1 with ZrO$_2$ loading at 30 vol% were stable and clear, and yielding a refractive index of 1.70. Due to the consequences of increasing viscosity with increasing NVC concentration, the M1142/NVC = 4/1 30 vol% ZrO$_2$ composites were selected as the optimal mixture. Figure 3.5b shows the optical dispersion curves of the cured composite resins, which is slightly higher than the uncured samples due to volume reduction during polymerization. M1142/NVC = 4/1 with 30 vol% ZrO$_2$ exhibits a refractive index above 1.7 over the whole visible spectrum with n$_D$, cured = 1.73.

The UV-Vis spectra in Figure 3.5c show that 150 µm films of various composite mixtures maintain good transparency over the visible spectrum. Pure NVC films result in the lowest transmittance values, while the M1142/NVC 4/1 with 30 vol% ZrO$_2$ possesses transparency above 85% in the visible region. The decrease of the transmittance in the M1142/NVC 4/1 with 30 vol% ZrO$_2$ can be rationalized by a small contribution of scattering from soft nanoparticle aggregates.

![Graphs and diagrams showing](image)

**Figure 3.5** Refractive index (n(λ) 589 nm) of M1142/NVC compositions with increasing ZrO$_2$ loading (a), refractive index versus wavelength of cured films of various compositions (b), and UV-Vis spectra of various cured 150 µm films (c).
These high refractive index resins were imprinted using a master mold with several different test patterns and pattern dimensions. As seen in the optical microscope images in Figure 3.6, there is no discernable difference between features imprinted in neat M1142 monomer and those imprinted using the M1142/NVC = 8/3.25 resin with 30 vol% ZrO$_2$ resins, which exhibits a substantially higher refractive index. The higher refractive index imprinting material shows greater potential for commercial optical devices and was therefore the focus of the roll-to-roll scale up manufacturing study.

**Figure 3.6** Optical images of manual imprints using M1142 with a) 0 vol% ZrO$_2$ and b) 30 vol% ZrO$_2$ and imprints of M1142/NVC 8/3.25 with c) 0% ZrO$_2$ and d) 30 vol% ZrO$_2$ Scale bars are 20 µm.
Two roll to roll trials were conducted using 5 vol% and 30 vol% ZrO$_2$ in M1142 using a variety of test patterns to determine the scope of the imprinting resin and performance. 5 vol% results are shown in figure 3.7 and the 30 vol% results are shown in Figure 8. Both were successful in replicating a broad range of geometry and scale from nanometer to micron and sub millimeter. Figure 3.8 illustrates the fidelity to the test pattern used for initial manual imprinting after 20 feet of run (6.1 meters).
Figure 3.8 Comparison of manual imprinting on glass (left, scale bar 20 um) to roll to roll imprints on PET (right, scale bar 50 um) after 20 feet of imprinting (6.1 meters).

For testing imprinting a larger scale, an electrowetting cell pattern and 10 um interleave pattern was used to investigate the ability to fill larger structures as well as maintain edge geometry. Figure 3.9 shows the ability fabricate large area structures with sharp edges even after 20 feet of run (6.1 meters).
For testing non-binary features with slanted walls, a pyramid structure was tested. Additionally, a cross pattern was also imprinted to broaden the scope of potential optical structures achievable with the composite resin. Figure 3.10 illustrates the large area fabrication of these structures after 20 feet of run (6.1 meters). With the smallest critical feature of 400 nm, making the design and showing no discernable shrinkage, the advantages of solvent free imprint materials can be demonstrated. While some roughness is observed under the smallest features, further optimization of the process to a single design provides better feature fidelity and decreased surface roughness as is demonstrated by the micropatterns in this experiment.
Figure 3.10 SEM images of 30 vol% ZrO₂ in M1142 roll to roll imprinted Pyramids (left) and crosses (right) after 20 feet of imprinting (6.1 meters). ImageJ measurements in b show the smallest critical dimension achieved of 400 nm, consistent with the fabricated master design, showing no discernable shrinkage.

3.4 Conclusions and future work

By controlling the composition of the Miramer monomer using high-refractive index nanoparticles and a high refractive index comonomer, the refractive index of the UV-curable resin could be increased from 1.58 to 1.73. By mixing the nanoparticle dispersion into the resin, or resin-NVC mixture, and then evaporating the solvent, we were able to achieve a homogeneous, transparent, solvent-free UV-curable material. Using UV-NIL, the high index resins were successfully patterned using stamps with critical dimensions of 400 nm. Imprinted patterns were
highly uniform over the patterned area and feature dimensions were consistent between different resin compositions. This solvent-free, high refractive index material is well suited for large-scale, roll-to-roll processing of patterned optical structures. R2R UV-NIL was conducted at 30 in/min (76.2 cm/min) line speed with flexible PDMS master mold and a variety of patterns were replicated successfully over a 20 ft test run (6.1 m).
CHAPTER 4

Scalable Nanoimprint Lithography Process for Manufacturing Visible Metasurfaces
Composed of High Aspect Ratio TiO$_2$ Meta-atoms

4.1 Introduction

Metalenses are ultrathin planar lenses comprising nanofeatures that efficiently diffract light, rivaling the performance of bulkier refractive components. In addition to making lenses more compact and lightweight, metalenses also possess more degrees of freedom than traditional optical elements, and can be designed to achieve a desired amplitude, phase, or polarization distributions by tuning size, shape, pitch and material properties. Complex functionalities can be achieved both with single-layer and multilayer metalenses, providing more utility in a smaller space than traditional refractive lenses. The manufacturability of metalenses and the potential sophistication of their designs make them promising candidates for the next generation of optics. Efficient metalenses rely on subwavelength elements with precise dimensions and small pitch, presenting challenges for scalable manufacture, particularly for lenses that operate in the visible or at shorter wavelengths. In this regime, critical dimensions are smaller than those achievable by photolithography, and thus electron-beam lithography (EBL) is often relied on to fabricate visible spectrum metasurfaces. EBL provides nanometer-scale precision but suffers from low throughput and high cost. The expense of extended tool use alone is prohibitive to commercial manufacturing of optical components, but the cost for large-scale manufacturing is made even more prohibitive by additional steps such as e-beam resist deposition, resist development, chemical vapor deposition, etching and cleaning that are used in the traditional fabrication of metalenses.

For structures at this length scale, nanoimprint lithography (NIL) is a promising alternative to EBL. NIL is a technique by which a resist is mechanically patterned using an elastomeric stamp.
containing the nanostructure template. The resist can then be cured and the elastomeric stamp released from the resist to leave a patterned structure. With NIL, a single master can be used to make many stamps, which in turn can be used to make 10-100 imprints each, drastically improving scalability.\textsuperscript{91,92} In some NIL processes, such as Liquid Transfer Imprint Lithography (LTIL) and NIL etch resists, a resist is imprinted to create a template into which a secondary material such as metal, metal oxide or polymer is deposited.\textsuperscript{93} Nanoscale optics have been successfully manufactured using these resist templating approaches and their variants.\textsuperscript{94–97} The imprinted resist is typically etched and backfilled with a secondary material before removal of the imprinted resist. The templated secondary material is realized after resist removal but requires multiple additive (secondary material deposition) and subtractive steps (etch or liftoff).

Traditional NIL, however, is a direct imprinting method in which the imprint material is developed to have the desired properties of the final device such as transparency, refractive index and structural stability. Because it is an additive technique, it requires neither sacrificial materials nor etching steps, streamlining manufacture. Formulating the imprint material for the specifications of the final patterned device enables single-step additive fabrication, reducing material waste, tool costs and manufacturing time as shown in Figure 4.1. Moreover, structures fabricated by direct-imprint NIL require minimal material and tool costs due to the small amount of imprint material required for additive manufacturing. Direct imprint techniques have been used to demonstrate various optical elements, including microring resonators\textsuperscript{98}, gratings,\textsuperscript{30,99} photonic crystals,\textsuperscript{30} structural color materials\textsuperscript{100} and metalenses.\textsuperscript{101}

NIL is commonly used with polymeric, sol-gel or composite resists to replicate a master with varying material properties.\textsuperscript{31} Polymeric materials typically are limited to low refractive indices, providing insufficient phase delay for metalenses to focus effectively. In the pursuit of
higher refractive indices, researchers have loaded polymeric resins with high refractive index nanoparticles, such as titanium dioxide or zirconium dioxide and have used these resins for imprinting optical elements. A recent work demonstrated a NIL process to fabricate metalenses using a nanoparticle-enhanced resin. However, titanium dioxide is a photooxidation catalyst that can react with the polymeric matrix and cause yellowing of the carbon content by successive oxidation. Over time, this yellowing leads to increased absorption and decreases the efficiency of the metalens.

Recently, we developed a variant of NIL for the direct fabrication of patterned inorganic devices using metal oxide nanoparticle-based inks. In this work, we use TiO$_2$ based
nanoparticle inks for the fabrication of high aspect ratio metalenses. Here, the photocatalytic ability of titanium dioxide is exploited during the UV-assisted cure of the NIL ink, resulting in an inorganic material. TiO$_2$ will not yellow over time, proving a distinct advantage over imprinting materials that contain polymers, and TiO$_2$ is self-cleaning. Moreover, the inorganic structure provides a high tensile modulus required to retain the high aspect ratio nanofeature geometry after stamp release. The refractive index of our NIL ink is 1.9, comparable to that of silicon nitride (n = 2.0), a material used for conventionally manufactured visible-wavelength metasurfaces. Using our nanoparticle-based NIL inks, metalenses traditionally requiring many steps are fabricated in a single step of direct-imprint NIL in under two minutes total process time and repeated >15 times with a single stamp. Reproducibility is quantitated by measuring the focusing efficiency of metalenses on successive imprints, which show consistent performance after 10 imprints.

4.2 Experimental Section
4.2.1 Design and Fabrication of Silicon Masters

All materials were purchased from Sigma Aldrich unless specified. Titanium dioxide nanocrystal solution 50 wt% in propylene glycol monomethyl ether acetate was purchased from Pixelligent Technologies LLC. Materials were used as received without further purification.
Master design curves, determined by a previously described method, are shown in Figure 4.2. Two metalens designs were present on the master used in this work: one with hexagonal posts in a triangular lattice with a lattice constant of 430 nm, and one with rectangular posts in a square lattice (375 nm lattice constant). Both designs are for nano-posts with a refractive index of $n = 1.9$ and height $h = 600$ nm that rest on a fused silica substrate ($n = 1.46$). Before creating the EBL mask, nano-post dimensions are scaled to account for an initially estimated 10% shrinkage in the imprint material. To account for potential errors in the fabrication of the master, five copies of the metalenses were fabricated by changing the nano-posts widths by -10 nm, -5 nm, 0, 5 nm, and 10...
Masters were fabricated on a 525-μm-thick silicon substrate. First, we defined the metalens pattern using a positive-tone electron beam resist (ZEP 520A-7, Zeon Chemicals) and 125 keV electron beam lithography system (ELS-F125, Elionix). To form a hard etch mask, we evaporated 50 nm of aluminum oxide on top of the sample and lifted it off in a solvent (Remove PG, Microchem) at 80°C. The pattern was then transferred to the silicon substrate by plasma etching in C₄F₈ and SF₆ gases. We removed the residual etch mask in a mixture of ammonium hydroxide and hydrogen peroxide heated to 80 °C. Two separate masters with similar designs were used in this study. Images in Figure 4.8a and Figure 4.9 and characterization data presented in Figure 4.9 were produced using one master design that was etched to a depth of 660 nm; images in Figure 4.8b and Figure 4.3 are of imprints produced using the second master that contained the test patterns and was etched to a depth of 605 nm.

![Cross-sectional SEM images](image)

**Figure 4.3** Cross-sectional SEM images with height and width measurements as well as the calculated aspect ratios achieved by direct NIL.

### 4.2.2 Stamp Fabrication

The fabricated master was cleaned with isopropanol (IPA) and compressed air followed by Ozone cleaning with a UVO 342 from Jelight Company Inc. to liberate any oils and reduce surface
energy for coating. The master was then transferred to a vacuum desiccator affixed with an empty 7-dram vial. 0.1 mL heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane from Gelest, Inc. was added to the vial and the desiccator was pumped down for 30s on a Schlenk line and sealed for 18-24 hours at room temperature. The master was removed and rinsed with IPA, water and then IPA again to ensure removal of any residual unbound material. The IPA is dried off with compressed air and the master was ready for stamp fabrication.

1.7g 7-8% vinyl methylsiloxane-dimethylsiloxane, 5 uL 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, 9 uL platinum-divinyltetramethyldisiloxane, and 5g toluene were added by mass balance and repeating micropipette to a glass vial and vortex mixed. 0.5 mL 25-30% methylhydrosiloxane-dimethylsiloxane was added and vortex mixed again until homogeneous by observation of refractive consistency.\(^{112}\) hPDMS was spin cast (3000 rpm, 40 s, 1500 rpm/s ramp rate) as the replication layer onto a fluorinated master surface cleaned with IPA and compressed air. The film was then thermally cured at 100º C for 45 minutes. The stress dissipation layer was a softer commercial PDMS, Sylgard 184. After mixing in a 10:1 wt ratio thoroughly, it was degassed under vacuum providing ample space for gas evolution and preventing any sulfur contamination which often poisons the platinum catalyst.

A 0.3 mm-glass backing of appropriate size was cut and the edges were reinforced with transparent tape. The glass surface was cleaned with IPA and a Kimwipe followed by deposition of 1,1,1,3,3,3-hexamethyldisilazane and coating with a Kimwipe. Four footers were cut in a beam shape from a single flat square section of Sylgard in order to support each corner of the master equally when face down on the glass backing. The footers were placed in position using the hPDMS coated and cured master to provide dimensions. The degassed Sylgard was then poured carefully into the center of the footers in order to prevent bubbles, pouring from close to the surface
and prevent any streams of PDMS with a Kimwipe. Directly after Sylgard deposition, tweezers were used to set one side of the master onto two of the footers and then slowly bring the angle down to the surface of the Sylgard. This ensures no bubbles form beneath the stamp surface. Pressing gently on the back of the master compresses the footers and locks the master in place by suction in order to prevent any sliding or slipping from the layer stack. The assembly was transferred on a flat surface to a 75 °C oven for 4–24 hours. After curing, the assembly was allowed to cool to room temperature before release. The edges of the master were freed from any PDMS overlap on the back with a razorblade. The edge of the stamp to master interface was lubricated with IPA while face down, the assembly was flipped so the master was face up, and then a tweezer was used to grip the master edge, while the stamp was gently removed in one slow fluid motion. The stamp was immediately rinsed with IPA to prevent any feature collapse due to capillary action from IPA drying. After the immediate IPA, water was used to remove the IPA without collapsing features. After drying any residual water on the stamp with compressed air, it was ready for use. The master should also be cleaned with IPA in preparation for the next stamp to be made. Currently, we have made over a dozen stamps from a single master.

4.2.3 preparation of Titania composite solutions, films, and imprints

A 50 wt% titanium dioxide nanocrystal solution was diluted with a stock solution of 0.15 wt% anionic surfactant in ethyl lactate to 10 wt%. A silane coupling agent was added in 15 wt% in relation to the mass of nanocrystal before vortex mixing and sonication for 15 min. The solution should also be re-sonicated for 15 min. and 0.45 µm filtered before use to ensure consistency in processing.

Silicon (or fused silica) wafers were cleaned with IPA and dried with compressed air before cleaving and cleaning with Ozone for 15 minutes. The solution was spin-coated at 4000 rpm for
3s with the ramp rate of 1500 rpm/s and then placed on a raised surface for 20 s before making stamp contact. The contact was made on one edge and then gently rolled with a fingertip across the wafer to completely remove any bubbles during the stamp placement. The assembly was transferred to a 365 nm pulsed UV source custom made by Carpe Diem Technologies. The pulsed UV conditions of 35 V 5 ms on, 15 ms off and 2000 repetitions over 40 s provide a fully cured imprint. The assembly was affixed to a vacuum chuck and the stamp was gently removed in one fluid slow motion, ensuring the stamp doesn’t make contact with the imprint again after released as it will damage the lenses. Following the same process, the stamp was reused 15 times or more. The imprints prepared on Si wafers and fused silica substrates were used for SEM analysis and focusing efficiency testing, respectively.

For the preparation of films for haze measurements, Si (or fused silica) wafers were cleaned as in preparation for imprinting. The solution was spin coated at 4000 rpm for 3 s with the ramp rate of 1500 rpm/s and allowed to air dry over 30 s. It was then UV cured using the same conditions with those for the imprints.

4.2.4 Characterization

Refractive index measurements of films were taken on a JA Woollam RC2 variable angle spectroscopic ellipsometer at 45-65° between wavelengths ranging from 450 nm to 1690 nm. Ellipsometric data was fit using the Cauchy transparent thin film on Si model in the CompleteEase software. Refractive index values reported are reported at λ = 543 nm. SEM images of imprints are taken on a FEI Magellan 400 FESEM and feature dimensions are measured using ImageJ software.

The lenses were illuminated by a Uniphase JDSU 1676 HeNe laser source with unpolarized collimated beam with wavelength of 543 nm. To image the metalenses’ focal spots, the focal plane
intensity distribution was relayed and magnified using a 50× objective lens and a tube lens with a focal length of 20 cm and was captured by a CCD (Figure 4.9c).

To measure the optical power focused by the metalens, the incident laser beam was partially focused using a 5 cm focal length lens to produce a Gaussian beam with a beam radius of ~117 μm (Figure 4.9g), ensuring all the laser power passes through the metalens aperture. The light focused by the metalens was relayed by a 10× objective lens and a tube lens with 20 cm focal length and was directed toward and measured by a power meter (ILX Lightwave OMM-6810B with an OMH-6722 power head) masked by an iris with a diameter of 100 μm in the image plane (corresponding to a ~10 μm diameter circle in the metalens focal plane). The power incident on the metalens was determined by measuring the power incident on the power meter when removing the sample and the iris and correcting it for Fresnel reflection of the backside interface of the fused silica substrate. The reported focusing efficiency values represent the ratios of the optical power focused by the metalens to the optical power incident on it.

The same approach was implemented to capture the image of the focal spot of the large-scale lens with 4 mm diameter. However, to provide a large incident beam with planar phase front at the device’s surface, a laser beam expander (Melles Griot 10X) was utilized. A 4-mm aperture was placed right before the device to ensure the same beam size reaching the lens. Due to the long focal length of the device, the focusing efficiency was measured at the real focal plane of the lens. Thus, a 10-μm-diameter pinhole was adjusted at the focal spot and the output power was measured with a power detector. The power incident on the metalens was determined by measuring the power incident on the power meter when removing the sample and the 10-μm pinhole and correcting it for Fresnel reflection of the backside interface of the fused silica substrate. The reported focusing
efficiency represents the ratio of the optical power focused by the metalens to the optical power incident on it.

The local diffraction efficiency of the 4-mm-diameter metalens was determined by focusing an incident beam with a lens with 5 cm focal length to illuminate a small region on the metalens (~90 μm diameter) and measuring the powers of incident beam and the first diffraction order using a power meter (ILX Lightwave OMM-6810B with an OMH-6722 power head). A schematic of this measurement is shown in Figure 4.4a. The beam deflection efficiency for different deflection angles, defined as the ratio of first diffraction order power to incident power, is shown in Figure 4.4b.

![Figure 4.4 Beam deflection efficiency.](image)

**Figure 4.4** Beam deflection efficiency. (a) Schematic of the measurement. A 90-μm-diameter incident beam illuminates a portion of the metalens that deflects to an angle \( \theta \). The deflection efficiency is the ratio of the powers in the first diffraction order and the incident beam. (b) Measured deflection efficiencies for the 4-mm-diameter lens (diamonds, dot-dashed lines), and simulated deflection efficiencies for 600-nm-tall nano-posts (triangles, solid lines) and 520-nm-tall nano-posts (circles, dashed lines) for s-polarized (blue) and p-polarized (orange) light. Trend lines are shown as a guide for the eye.
The transmittance and haze of the imprint material films were measured using a 632.8-nm helium-neon laser (JDS Uniphase 1122) and an integrating sphere (Newport 819-IS-2). Figure 4.5 shows a schematic of the measurement setup. We measured the total transmitted power by placing the sample in front of the integrating sphere with its through port closed. To measure diffuse transmittance (haze), the through port was opened to let the unscattered light to pass through. The ratio of the scattered power to the total transmitted power was ~0.31%, demonstrating a negligible scattering by the titanium dioxide nanoparticles.

**Figure 4.5** Optical haze measurement. The percentage of light scattered by the film was measured using an integrating sphere and a power detector (PD). (a) The direct transmission measurement. (b) The haze measurement.

### 4.2.5 Metalens and beam deflector simulations

To determine what focusing efficiency can be expected, we performed simulations of a cylindrical lens designed using the design curve for rectangular nano-posts shown in Figure 4.2. A cylindrical lens captures the fundamental behavior of the design while keeping the simulated
volume and required computational resources small. The simulated lens has a focal length of 735 μm and NA = 0.2. In the simulations, the lens is illuminated from below by a normally-incident plane wave with a free-space wavelength of 550 nm. Fields are traversing the metalens are simulated using a freely available finite-difference time domain (FDTD) solver\textsuperscript{113} at 13 nm resolution and then propagated from a plane near the metalens to its focal plane using a Fourier technique. The focusing efficiency of the cylindrical lens is here defined as the fraction of incident power which passes through a 5.5-μm-wide slit in the focal plane. Figure 4.5 shows a schematic of the simulation. As designed, the simulated efficiencies for the metalens are 73.4% and 74.4% for $p$- and $s$-polarized incident fields, respectively. In the main text we report the rounded average of these two polarizations.

![Cylindrical lens simulations](image)

**Figure 4.6** Cylindrical lens simulations. A 300-μm-wide cylindrical lens with NA of 0.2 designed using the curve for rectangular nano-posts in Figure 4.2 was simulated using an FDTD solver. Efficiency is defined as the fraction of incident power that passes through a 5.5-μm-wide slit in the focal plane.

Discrepancies between the simulated and measured efficiencies can be attributed primarily to differences in the designed ($h = 600$ nm) and realized ($h = 520$ nm) nano-post heights; to the
presence of a 75-nm-thick residual layer of imprint material between the nano-posts and fused silica substrate, which is not accounted for in the design; and to point defects in the imprint material, which produce undesired scattering. Simulated focusing efficiencies of the cylindrical lens with shorter posts and no residual layer, with posts of nominal height and 75-nm-thick residual layer, and with the combination of these two nonidealities are 61.3%, 57.7%, and 52.8% for \( p \)-polarized incident light and 62.3%, 58.4% and 55.3% for \( s \)-polarized incident light, respectively. Height errors in the nano-posts produce wavefront error but do not reduce the transmittance of the lens significantly: the fraction of power transmitted through the lens with 520-nm-tall nano-posts is 92.4% for \( p \)-polarized incident light and 93.7% for \( s \)-polarized incident light, close to the corresponding transmittances of 96.1% and 97.2% for the lens with 600-nm-tall nano-posts. A 75-nm-thick residual layer reduces the transmittances to 78.3% and 80.2% for the lens with nominal nano-post heights and to 78.2% and 82.0% for the lens with shorter nano-posts. As we mention in the text, the effect of the residual layer is thickness-dependent, and transmittance can be increased by controlling this thickness.

We used the grating averaging technique\textsuperscript{111} to determine the ideal deflection efficiency for beam deflectors derived from the hexagonal nanopost design. The deflection efficiencies for both 600-nm-tall nano-posts (nominal height) and 520-nm-tall nanoposts are presented alongside measured local deflection efficiencies for the 4-mm metalens in Figure 4.4b.

4.3 Results and Discussion

The direct-imprint NIL process is a replication process by which a stamp inverts the patterns of a master, which is then reinverted into the imprint material to provide the original structure from the master as seen in Figure 4.7. The nanoimprint stamps in this work were cast on a silicon master mold. Details of the master design are given above. The master consists of 740-
nm-tall nano-posts etched into a silicon substrate and was patterned via EBL and reactive ion etching. The metalenses on the master are designed for a wavelength of 550 nm by assuming a minimum feature size of 120 nm (post width and gaps), a maximum aspect ratio of five, a refractive index of 1.9 for the meta-atoms, and by using the curves shown in Figure 4.2 that were determined via the grating averaging technique. The nano-posts are assumed to be 600 nm tall and rest on a fused silica substrate. Two different metalens designs are present on the master: one with hexagonal nano-posts and one with rectangular nano-posts (see Figure 4.2). In designing the master we assumed a 10% shrinkage of the features expected during the NIL replication process and scaled nano-post dimensions accordingly.
Prior to stamp fabrication, the master was fluorinated to reduce adhesion during the stamp making process, which can help successful transfer of nanofeatures with high fidelity. To make a stamp, an hPDMS film is cast onto the master, thermally cured, and placed face down into a thermally curing silicone elastomer (Sylgard 184) with a glass backing as mentioned in the experimental. After thermally curing the silicone elastomer, the stamp is released from the master and used directly for imprinting. Lubrication with isopropanol aids the stamp’s release from the

**Figure 4.7** Fabrication of lenses by an inorganic direct imprint method (a) hPDMS stamp fabrication (b) Spin coating and stamp placement, followed by irradiation with a pulsed UV source and successive release to reveal the lens structure. (c) Resulting series of imprints 1 through 10.
master without breaking higher aspect ratio features. Following this procedure, the master can be used to make additional stamps.

Metalenses are cast by imprinting a titanium dioxide nanocrystal solution and curing it using pulsed UV. The solution is formulated to ensure fluidity after spin coating and proper sol-gel binder selection for increased feature retention. After gentle and consistent lamination of the stamp, the assembly is moved to a pulsed 365 nm LED UV tool to cure the imprint. Pulsed UV enables a low thermal cure requirement ensuring low residual thermal stress. The pause between

Figure 4.8 SEM characterization of stamp lifetime imprinting performance on silicon. (a) Side by side comparison of the master with the imprinted samples 1, 10 and 15. A 20% shrinkage is observed in the composite imprints as is consistent with the literature and was partially accounted for in the master design. (b) Imprint 15 from a similar master is shown with cross sectional images.
pulses facilitates the transport of thermal energy converted by the UV absorption of titanium dioxide to dissipate away from the surface instead of into the substrate. A lower residual stress also facilitates alignment by reducing the extent by which the two materials (substrate and imprint) thermally expand by reducing the thermal input into the substrate. After UV curing, the stamp can be released, taking care to ensure that the stamp does not make contact with the features after release. Due to the strain rate dependence of the mechanical properties of the stamp materials and the brittle nature of inorganic materials, a slow release rate is highly favorable for the imprint quality.

To avoid using a polymer matrix, sol-gel small molecule binder moieties were used in the imprint material formulation. Sol-gel imprint materials alone suffer from excessive shrinkage, high residual stress that compromises mechanical integrity or cracking, but by loading with the appropriate nanocrystals, shrinkage can be reduced from 90% to 10% without cracking. We cure the imprint material with a high-intensity pulsed UV LED array, which provides sufficient local irradiation to react at the titanium dioxide nanocrystal surface and form the inorganic sol-gel linkages.

A stamp lifetime experiment was conducted to demonstrate the durability of the stamp over multiple imprints. Figure 4.8 shows SEM images of the master and imprints 1, 10 and 15 that were manually fabricated using a single stamp in 30 minutes. Upon close inspection, it can be seen that nearly every single nano-post is intact as indicated by a consistent bright sidewall as is common in SEM of vertical features. The absence of broken features after an extended imprint trial demonstrates the imprint material’s mechanical strength after curing. Moreover, Figure 4.8 confirms that the imprinted features show minimal distortion and that gaps as small as 136 nm between the nano-posts have been successfully obtained. Measurements of the cross-sectional
SEM images revealed aspect ratios up to 7.8 for the imprinted nano-posts. While potentially more imprints per stamp could be achieved, this study demonstrates feature fidelity and stamp performance are tolerant of at least 15 imprints without significant deterioration. To further explore the limits of the imprinting processes aspect ratio and feature size, a second master containing test patterns composed of nano-posts with dimensions as small as ~60 nm was patterned and etched to a different depth. Using the second master we were able to reliably imprint nano-posts with widths as small as ~57 nm and aspect ratios up to 8.4 as shown in Figure 4.3.
Figure 4.9 Characterization of the metalenses. (a) Schematic of the fabricated metalenses. (b) Optical micrographs of imprints 1, 5 and 10. Scale bar, 100 μm. (c) The image of the fabricated 4 mm-diameter lens and its corresponding focal spot when the device is illuminated with source at a far distance (plane wave incidence). (d) Illustration of the measurement setup for characterizing metalenses’ focal spots. (e) Focal spot images for imprints 1, 5 and 10 and the 4-mm diameter lens. Scale bar, 2 μm. (f) Line cuts of centers of focal spots shown in (d). The focal spot of an ideal metalens (Airy function) is also presented. (g) On-axis modulation transfer functions (MTF) for different imprints. The ideal MTF is also shown for comparison. (h) Illustration of the measurement setup for characterization of metalenses’ efficiencies shown in (b). (i) Illustration of the measurement setup for characterization of the large-scale metalens’ efficiency shown in (c).
A schematic of the imprinted metalenses is illustrated in Figure 4.9a. Metalenses have a diameter of 400 µm and a focal length of 980 µm (i.e. NA=0.2). Figure 4.9b shows optical micrographs of imprints 1, 5 and 10. As a proof of concept, to manifest that this method can also be successfully used for large-scale devices, a lens with 4 mm diameter and focal length of ~9.8 mm (NA=0.2) was fabricated with the same approach. Figure 4.9c presents this large-scale lens and its corresponding focal spot when it is illuminated with an LED pointer working with a wavelength of 520 nm and located at a far distance (infinity) to provide a planar phase front of the incident light at the surface of the device. Movie S1 presents a video of the focusing.

The metalenses were characterized by illuminating them with a collimated laser beam and recording their focal spot intensity distributions using the setup shown in Figure 4.9d. Due to the large area of the 4 mm-diameter lens, a laser beam expander was adjusted instead of the tube lens behind the device to provide a large, collimated beam. The metalens focal spots are magnified by the objective and tube lenses, captured using the camera, and are presented in Figure 4.9e. Line cuts of the measured focal spot intensities of the metalenses with hexagonal nano-posts and the corresponding curve for an ideal lens (Airy function) are shown in Figure 4.9f, and the on-axis modulation transfer functions (MTF) for these metalenses are presented in Figure 4.9g. As the measured focal plane intensities and MTFs show, the imprinted metalenses are nearly diffraction limited.

The focusing efficiency, here defined as the fraction of incident power that passes through a 10-µm-diameter pinhole in the focal plane, was measured using the setup shown in Figure 4.9h. The measured focusing efficiencies for imprints 1, 5, 10 of the metalenses with hexagonal nano-posts were 55%, 54% and 57%, respectively, and for the metalenses with rectangular nano-posts were 49%, 50% and 55%, respectively. The efficiency of the 4-mm-diameter lens was measured
at the focal plane by adjusting a 10-μm-diameter pinhole and a power detector at the focal spot. The setup is shown in Figure 4.9i. The measured focusing efficiency was 43%. As a point of comparison, the focusing efficiency of an NA=0.5 metalens formed of silicon nitride nano-posts and produced by conventional methods (EBL and plasma etching) was reported to be 63%.108

To benchmark our measurement results, we simulated 300-μm-wide cylindrical lenses with the same NA based on the rectangular nano-post design. A schematic of this simulation is shown in Figure 4.6. These simulations give information both about the maximum efficiency of the metalens design and about how geometric deviations from it impact metalens performance. The experimentally realized metalenses differ from the design in two ways: the realized nano-post heights are shorter (520 nm vs. 600 nm), and there is a thin (ca. 75 nm) residual layer of imprint material that the design does not account for.

In simulation, a cylindrical lens with the nano-post heights and residual layer present in the imprints has a focusing efficiency of 54%, consistent with our measured results. As designed (i.e., with 600-nm-tall nano-posts and no residual layer) the simulated focusing efficiency is 74%. To separate the effects of the shortened nano-posts and the residual layer, we ran two additional simulations: one with 520-nm-tall nano-posts and no residual, which gives a focusing efficiency of 62%; and one with nano-posts with nominal height and a 75-nm-thick residual, which gives an efficiency of 58%.

These two nonidealities affect the metalens performance in different ways. Even at nominal nano-post height, the metalenses have only partial phase coverage (see Figure 4.2a–b), and shorter nano-posts further reduce the phase coverage, producing wavefront error. The residual layer of imprint material acts primarily through thin-film interference, which at this specific thickness increases the reflection of the metalenses. Understanding these two effects will allow us to address
them in future imprint trials: taller imprinted nano-posts should be achievable by etching the silicon master to a greater depth, and the transmittance of the metalenses should be improved by either decreasing or increasing the thickness of the residual imprint material by tuning the weight percent of nanoparticles in solution. Details of these simulations are presented in the Metalens and beam deflector simulations section.

We also used the 4-mm-diameter lens to experimentally determine the deflection efficiency, defined as the ratio of the power in the deflected beam to the incident power, at different locations across its aperture. For comparison, we simulated a series of beam deflectors with similar deflection angles to determine the ideal deflection efficiencies for our design. A similar study is presented in ref. 111. A schematic of this measurement and efficiency data are shown in Figure 4.4, and detailed descriptions of both measurement and simulation are given in the Metalens and beam deflector simulations section.

Finally, to evaluate the effect of potential scattering caused by the porosity of the imprint material on the metalens efficiency, we measured the percentage of diffuse scattered light (haze) for an unpatterned layer of the imprint material and found it to be 0.31%, sufficiently below the haze-limited regime (Figure 4.5). Thus, the porosity of the imprint material has a negligible effect on the metalens performance.

As a proof of concept for slanted grating, another target device design for high refractive index optics, the solution used for the fabrication of metalenses was diluted to 10 wt% to accommodate for the shorter feature size. With slanted gratings, chipping or breakage of the fin tips is the most common challenge, and with this direct imprint approach, large areas of defect free slanted gratings can be fabricated. Furthermore, the minimal shrinkage ensures the nanofeature geometries and dimensions are conserved as can be seen in Figure 4.10.
Figure 4.10 SEM characterization of slanted gratings, imprinted with the same solid ratios, but diluted to 10 wt%. Analysis shows good large area replication and sharp well defined fine tips and geometries.

4.4 Conclusions and future work

With minimal defects or individual feature damage or deviation, the stamp lifetime experiment indicates that a commercial scale tool could provide an even larger number of imprints per stamp due to more refined pneumatic control. The stamp can be applied between 15-20 seconds as is designed to function in currently scalable NIL tools.\textsuperscript{114,115} This pause time facilitates the transfer in the tool from the spin coating chuck to the alignment and imprinting module of the tool. A similar pulsed irradiation source can be incorporated into many commercial-scale imprinting
tools as there is often already a continuous UV source. This has the potential to enable higher precision backside alignment of these nanofeatures as well as multilayered lens alignment.

The focusing efficiency of metasurfaces fabricated using the proposed technique is currently limited by the refractive index, aspect ratio, and the presence of a residual layer. More efficient metasurfaces can be realized by relaxing the design constraints based on the minimum feature sizes and maximum aspect ratios that could be reliably fabricated using this technique. The test patterns we fabricated demonstrated that post widths and gaps as small as 60 nm and 100 nm, respectively, and aspect ratios as high as 8.4 are reliably achievable. Similarly, boosting the refractive index of the meta-atoms, either by reformulating the NIL ink or by post-imprint treatments, could enable metalenses with higher efficiency or NA. Finally, the inclusion of the effect of the residual layer in the design of metasurfaces can further increase device efficiency.

Utilizing the power of nanocrystals to boost the refractive index, as well as the catalytic photooxidation reactivity of titanium dioxide to provide a cure mechanism, an inorganic structure can be fabricated in a single step. Due to the speed of the curing process, imprints can be fabricated in 2 minutes, allowing for 30 wafer per hour manufacturing rate, enabling high-throughput and low-cost manufacture of optical metasurfaces thus paving the way for their widespread use.
CHAPTER 5
Selective Metallization and nanopatterning of High Refractive Index Microparticles for Colloidal Inks

5.1 Introduction

Coating systems have a rich history of development through scalability, improved optical performance, extended durability and ease of use. Colloidal inks for coating applications range in their composition from inorganic, organic and metallic colloids in polymeric, monomeric or inorganic matrix materials. Each material selection is critical to the final application, such as the desired finish being highly reflective, glossy or mat as well as the required thermal stability of the matrix and colloids for applications in the automotive and aerospace industries. For metallic coatings, metal colloids are used to coat the surface followed by heating and polishing in order to fuse and planarize the coating for optimal reflectivity. The breadth of accessible materials for coating materials is wider than it has ever been and as a result, composites have come to dominate the space.\textsuperscript{25} The key advantage to composites is the ability to tune individual components to achieve the desired optical outcome. Composites are often comprised of a polymeric, silicate or prepolymeric base and a colloidal system to improve mechanical, absorption, and scattering properties. Titanium dioxide is one of the most commonly used materials for coating systems due to its superior durability, and a high refractive index leading to ideal scattering properties.\textsuperscript{26} Many formulators have demonstrated work where altering the shape and size of colloidal or patterned components are able to change the scattering and other optical properties such as polarization and absorption.\textsuperscript{27} Additionally, research into the improvement of optical properties from colloidal orientation, and anisotropy has been investigated as well.\textsuperscript{28,29}
Metallized colloidal systems enter a new set of tunable parameters as it increases the reflection at select interfaces and emphasizes any anisotropy in the system depending on the number of metallized facets. Combination of metallization, orientation and dispersion gives an arsenal of tools for making custom shaped colloids with control over the optical properties over desired facets. Hybrid systems which combine metalized facets with high refractive index colloids allow for a combination of the material properties where specific spectral ranges can be controlled by varying the metal facets.

NIL is a common technique for the fabrication of micro and nanofeatures due to it high throughput and high precision. The recent development of nanoparticle composite imprint materials has afforded accessibility to the rapid manufacturing of titanium dioxide as well as many other metal oxides in micro and nanopatterning.\textsuperscript{30,31,57,106,118} The innovation behind titanium dioxide nanocrystal composites comes from their high loading of sub 20 nm crystalline nanoparticles, resulting in high refractive index materials with low haze that can be patterned readily.\textsuperscript{102} Additionally, their high density and inorganic binder provide good mechanical stability for free standing structures required in colloids. NIL provides a high throughput manufacturing scheme for tailorable shape and size colloidal systems for sharp edges and good feature definition. While research has been done to add structural color to pigmented inks, few reports show the use of NIL to provide the structural color element in colloidal inks.\textsuperscript{122}

In this work, titania pyramids are fabricated by NIL and selectively metallized on top and bottom facets with platinum and highly absorptive black nickel (B-Ni). The optical effects from metalized and native microparticles are assessed in coating composites to determine their compatibility with traditional coating systems and the influence of the metallization optical properties. With a metal evaporation, sputtering or electroplating step that can be dropped in place
at any point in the fabrication flow, the potential combinations of structure achievable provides a wide range for the broad market of applications. While only few structures and layers have been studied for these systems, potential for more sophisticated microstructures from NIL could open avenues to engineering colloids with nanometer precision.

5.2 Experimental Section

5.2.1 Master and stamp preparation

All materials unless specified are purchased from Sigma Alderich and used without further purification. Titanium dioxide nanoparticle solution 50 wt% in propylene glycol monomethylester acetate is purchased from Pixelligent Technologies LLC. Fluorolink MD700 and Vertrel xF were obtained from Fluorolink and BASF, respectively.

A NIL Technologies inverted pyramid master was fluorinated according to the literature with 70-100 uL of Heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane from Gelest, Inc. in a vacuum desiccator overnight. The Si master is removed, washed with IPA, water and then IPA again to ensure any residue that is not covalently bound is removed. The hPDMS was formulated following the literature and spin coated at 3000pm for 40 seconds followed by curing at 100ºC for 45 minutes. It is then assembled with a glass backing and Sylgard 184 cushion layer in a 10:1 weight ratio, being careful to prevent trapping bubbles and the Sylgard 184 is cured for 4-24 hours at 75ºC.

The master can be replicated by spin coating PFPE prepolymer comprised of 37% Vertrel xF, 60% Fluorolink MD700 and 3% 2,2 dimethoxy-2-phenyl acetophenone at 2000 rpm for 10s and then UV cured at 35V 5 ms on 15 ms off for 2000 repetitions with the top face exposed to oxygen in order to prevent full polymerization at the top interface. 1-2 mL of Norland Optical adhesive 60 is deposited to the center of the PFPE coated Si Master and a piece of PET is laminated
above the Norland, squeezing out any bubbles. The layer stack is UV cured once again at the same conditions to ensure the covalent bonding of all the layers except the fluorinated interface with the master. The PFPE inversion is then released from the edges gently. The edges of the PFPE inversions can then be trimmed to make a flat substrate for stamp making. hPDMS stamp fabrication is conducted according to the literature, taking specific caution of releasing the PFPE copies due to the rough edges of the films being encased or adhering to the hPDMS. This can cause delamination of the PFPE copy from the PET substrate if done improperly.

5.2.2 Film and composite deposition

For the Preparation of PVA films, 10g Mowiol® 4-88 was dissolve in 90g of deionized water overnight at room temperature with stirring. The solution is 1 um filtered and spin coated at 2000 rpm for 1 minute at 1500 ramp rate. The films show little change from thermal annealing.

For the preparation of PMMA films, 120 kDA PMMA is dissolved in anisole overnight at room temperature with stirring. The solution can be spin coated directly to Si wafer or above PVA film at 2000 rpm for 1 minute at 1500 ramp rate and annealed at 200ºC for 10 minutes to remove residual solvent. For nanopatterned PMMA release layers, the PMMA film is then thermally imprinted in a Nanonex NX-2608A at process conditions of 2-minutes, 180ºC and 120 psi.

For the preparation of Composites, A 50 wt% titania nanoparticle solution is diluted with a stock solution of ethyl lactate and FS66 to 10 wt%. 15 wt% relative to solids of sol-gel binder is added before vortex mixing and sonication for 15 minutes. The solution is spin coated at 4000 rpm for 3s at 1500 ramp rate above PMMA, PVA or Si. This solution can also be imprinted to achieve protruding titania pyramids.
5.2.3 Nanopatterning, backfilling, sputtering and electroplating films

For Nanopatterned Films, PMMA/PVA films are placed in the Nanonex NX-2608A in contact with the stamp. The nanonex is programmed to conduct a thermal imprint with a 2-minute pre imprint condition of 180°C and 120 psi to ensure thermal transport and equilibrated stamp contact. The imprint is then conducted at 250 psi and 180°C for 1 minute before cooling to 50°C and then release of pressure to ensure the solidification of the features before release.

A 50 wt% titania nanoparticle solution is diluted with a stock solution with ethyl lactate and FS66 to 25 wt%. The PMMA/PVA imprints are then spin coated with 25 wt% titania solution and UV cured with a custom pulsed UV LED source at 365 nm from Carpe Diem Technologies. The LED source operates at 35V 5 ms on 15 ms off for 2000 repetitions, totaling 45 seconds. A Cressington Sputter Coater CR208 provides platinum at a rate of 1 nm per minute and is sputtered for 5 or 10 minutes to achieve 5 or 10 nm of platinum, respectively.

The sputtered platinum layer is used as an electrode for electroplating sulfur and zinc doped nickel from a plating solution of 59.9 g/L nickel ammonium sulfate, 7.48 g/L zinc sulfate, 14.97 g/L sodium thiocyanate with a nickel foil counter electrode. The electroplating was conducted at 95°C, 2.25 V and 0.008 to 0.016 mA for 30 minutes to achieve 4 um thick black-nickel films.

5.2.4 Pattern release, dispersion and formulation

Patterns are submerged in water to release from PVA coated wafers and in anisole or acetone for PMMA coated wafers. The solutions can be sonicated for 5 minutes to break up platelets or concentrated by evaporation to achieve the desired wt%. Samples for SEM characterization were drop cast on Si wafers and dried at 60°C.

The dispersion afforded from the release step can be mixed with a compatible photoresist such as Norland optical adhesive 81 (NOA81). For these formulations, PMMA was used as a
release layer in order to be miscible with the NOA81 after release. After mixing with ~80 wt% NOA81, the solution is concentrated to afford a viscous dispersion. The solution is then drop cast or spin coated at 2000 rpm, 1500 ramp rate for 30 seconds and cured using the pulse UV tool at 35V 5 ms on 15 ms off for 2000 repetitions. Samples for VASE measurements were spin coated on glass and samples for UV/Vis/NIR were drop cast on glass to a coating thickness of 550 µm, 650 µm, 740 µm and 270 µm for NOA81, TiO₂ pyramids, pt coated TiO₂ pyramids and black nickel plated pyramids, respectively.

5.2.5 Characterization methods

The refractive index at λ = 632 nm of the titania composite films were measured using a JA Woollam RC2 variable angle spectroscopic ellipsometer. Ellipsometric data was obtained with angles of 55°-75° by 5° and fit using the Cauchy model in the CompleteEase software within the transparent range (450 nm to 1690 nm). EDX, cross sectional and top-down SEM images are obtained on a FEI Magellan 400 FESEM and measured using imageJ image processing software. UV/Vis/ IR was performed on a Perkin Elmer Lambda 1050 with an InGaAs integration sphere in order to conduct haze and transmission measurements.

5.3 Results and Discussion

For studying the optical effect of metallized and unmetallized pyramids, a common photoresist (NOA81) was loaded with three types of colloidal particles: unmetallized titania pyramids, titanium pyramids with 10 nm platinum on 4 facets and titanium pyramids with 4 µm black-nickel plating on one facet. For the unmetallized and platinum coated titania pyramids, the pyramids are imprinted directly above a release layer in order to release the colloids after UV
curing (Figure 5.1). The pyramids can be platinum sputtered after imprinting and before release for the 4-facet coating.

![Diagram of imprinting process]

**Figure 5.1** Process flow for the fabrication of selective metallization on four faces, redispersion, formulation and deposition onto surface

The imprint is cured with a pulsed UV system through the stamp, utilizing the catalytic photooxidation reactivity of titania.\(^{10-14,17,18}\) The nanocrystals are sub 20 nm to ensure no haze of scattering, making an ideal optical grade final structure.\(^{100}\) The stamp can then be released to realize the titania imprints, which can be sputtered before or after fabrication to provide single or multifaceted metallization as seen in Figure 5.2, 5.3, 5.4 and 5.5. These can also be released from the substrate with a solvent compatible with the release layer and re-dispersed into coatings.
**Figure 5.2** As Imprinted Titania pyramids above Pt sputtered PVA release layer for single face metallization (bottom right) and with good large area replication (top left).

**Figure 5.3** Cross sectional images of single facet coated 10 nm Pt coated Pyramids with dense titania core, above PVA release layer.
Figure 5.4 EDX cross sectional image of 10 nm Pt coated Titania pyramids mapping the presence of titanium (blue), platinum (white), carbon (red) and oxygen (green). Note the high oxygen and titanium in the pyramids while carbon content is low. Carbon content is high in the PVA release layer due to its organic nature.

Figure 5.4 shows the EDX of the titania pyramids coated with Pt, shown to be distributed on the surface of the 4 facets of the pyramids. Cleaving of the brittle titania core can be visualized in the SEM image, while some rough edges and minor underfilling can also be observed in the side walls, due to the 15% shrinkage of the imprint material. The platinum is mapped purely on the top surface and the absence of signal near the base of the pyramid provides evidence of one unmetallized face. The carbon rich polymer shows an abundant signal at the pyramid base to substrate interface, but minimal carbon content is observed in the pyramid itself, providing
evidence of a nearly all inorganic structure. The abundance of titania and oxygen mapped in the pyramid regions also confirms this.

**Figure 5.5** Platelets formed after release in water, and redeposition by evaporation on Si wafer (top). Isolated pyramids formed after 5-minute sonication of the released dispersion (bottom).

Having fabricated these metallized structures on a release layer, they are designed to be submerged in a small amount of solvent to form platelets. As released, with little agitation, the water can be redeposited onto a substrate with flexible platelets that can fold and reorient, similar to liquid transfer imprint lithography (LTIL) where a pattern is released and transferred onto another substrate, but this process is often fraught with defects due to the invariability of surface tension across a thin film. In order to make stand-alone individual pyramids, 5 minutes of sonication is used to break up the platelets. It was noticed that 10 minutes of sonication can lead to the breaking up of particles primarily by the mechanism of chipped edges, rounding the individual pyramids. Individual selectively metallized pyramids can be seen in Figure 5.5 where all orientations can be visualized, as well as some debris from the thin planar titania film from the
imprint residual layer. The nanocrystals are sub 20 nm to ensure no haze of scattering, making an ideal optical grade final structure.\textsuperscript{100}

\textbf{Figure 5.6} Structure color containing pyramids with 500 nm line patterns imprinted into the release layer.

In order to test the feasibility of accessing nanopatterned colloids, 500 nm line patterns were thermally imprinted into a PMMA imprint layer before the titania imprinting step. Upon release, single, paired and ribbons of pyramids with structural color elements were able to be imaged by SEM (Figure 5.6). While this proof of concept indicates the ability to nanopattern onto these engineered colloids, the deviation in pitch of the imprinted 500 nm lines causes broadening of the absorption peak. It’s hypothesized that smaller nanofeatures and larger micro pyramids would provide a narrower absorption band.
**Figure 5.7** Fabrication scheme for titania pyramid structures on black, highly absorptive nickel platelets.

For thermal imprinting of inverted pyramids (Figure 5.7), the PDMS stamp was placed face down on the film stack and loaded into the Nanonex. The imprint is conducted at 250 psi and 180°C to achieve the desired depth of imprint. The assembly is removed from the nanonex and the stamp is released to reveal the polymeric imprints, which can then be sputtered with platinum and backfilled with titania or backfilled with titania and sputtered successively (Figure 5.8, 5.9 and 5.10).
**Figure 5.8** Process flow for the selective metallization of inverted titania pyramids with the added benefit of having an etchable intermediate structure.

**Figure 5.9** Top down and cross-sectional image of PVA/PMMA imprinted inverted pyramids with Pt sputtering before backfilling. Dimples at the deepest pyramid points is inherent to the process and a higher degree of filling simply thickens the layer instead of filling in dimples.
Figure 5.10 EDX cross sectional image of 10 nm Pt coated PMMA/PVA inverted pyramids backfilled with titania, mapping the presence of titanium (cyan), platinum (white), carbon (red) and oxygen (blue). Note the high oxygen and titanium in the pyramids while carbon content is low. Carbon content is high in the PVA release layer due to its organic nature.

In order to confirm the presence and isolation of platinum on the four selected faces of the inverted pyramid, EDX mapping was conducted on a PVA/PMMA imprint titania backfilled sample cross section (Figure 5.10). The elemental mapping shows a clear abundance of titanium and oxygen in the core of the inverted pyramid. The carbon content of the polymeric films and silicon content of the substrate can be visualized as well. A clear outline of platinum surrounding the interface between the high refractive index titania and low refractive index polymer indicated
a successful metallization of four faces. The absence of signal at the surface of the pyramid shows the fifth face is left unmetallized. The structures demonstrate an ideally ordered and metallized surface with high performance optical grade materials for custom optical properties with high resolution and feature fidelity.

In order to have greater control over the visible spectrum, black-nickel plating was investigated to provide a highly absorptive, less reflective metallized surface. Black nickel differs from other nickel-plating procedures by incorporating zinc and sulfur dopants that change the absorption of the material across the visible spectrum. Samples of stainless steel were plated with black nickel to observe the change in reflection from the black nickel coating (Figure 5.11). The reflectance of the black-nickel plated stainless steel decreased greatly indicating an increase in the absorption. For the fabrication of the colloidal samples, the inverted pyramid approach from Figure 5.7 is used to metallize a single face with platinum and then electroplated from the platinum layer to provide the black-nickel plated film above the titania pyramids. Due to the thickness of the plated films, isolated pyramids were not achieved even after sonication. The released nickel platelets can be seen in Figure 5.12 where the platinum layer can be seen to separate the titania domains from the black-nickel film.
Figure 5.11 UV/Vis/IR in reflection mode, showing increased absorption from black-nickel coating (blue) compared to stainless steel substrate (orange).

Figure 5.12 SEM imaging of the selectively black-nickel plated patterns for colloidal pigments in top down (top) and cross section (bottom). Red arrow indicates the 10 nm platinum boundary between titania and nickel.
To confirm the localization of the components of the microstructure, EDX elemental mapping was conducted on the black-nickel plated samples (Figure 5.13). In can readily be seen that the titania domains are clearly defined within the pyramid structure, where the black nickel is exclusively seen outside of the pyramid regions. The black nickel shows a strong sulfur signal and a modest nickel signal due to the conductivities and required excitation voltages for each element. Additionally, shadowing from the detector can be visualized in the oxygen signal with a shadow in the bottom left of the image on the far side from the detector. The black-nickel platelets were observed to orient in all directions, with a preference to being vertically oriented due to the highly dense nickel film (Figure 5.14).

Figure 5.13 EDX image of titania pyramid structures on black, highly absorptive nickel platelets, mapping the presence of sulfur (yellow), nickel (magenta), titanium (cyan) and oxygen (blue). A
shadow away from the detector can be observed in the oxygen signal. Titania regions appear to be isolate. Sulfur dopants in the black nickel give stronger signal than nickel due to their lower conductivity.

![Figure 5.14 Optical profilometry image of the cured composite photoresist, showing protruding structures and upright structure.](image)

After successful fabrication and characterization of the layers, the three colloids of study were prepared for formulation into NOA81. Unmetallized titania pyramids, titanium pyramids with 10 nm platinum on 4 facets and titanium pyramids with 4 um black-nickel plating on one facet were individually loaded at 20 wt% into NOA81 from their released dispersions in acetone.
and concentrated to afford the viscous dispersion. Measurements on the VASE (Figure 5.15) show no change in the bulk refractive index, but an increase in the modelled absorption for the titania and pt coated titania samples. VASE data for black-nickel plated colloidal samples was not able to be modelled with good fitting error due to the high level of scattering and absorption.

![Figure 5.15](image)

**Figure 5.15** Variable angle spectroscopic ellipsometry data modeled with a Cauchy transparent thin films model, expanded using a transparent B-spline to obtain the refractive index (n, left) and absorption (k, right).

The haze and transmission of these colloid loaded photopolymer composites show an expected trend between material selection and optical response (Figure 5.16). The photopolymer itself shows high optical transparency across the spectrum except for below 300 nm and above 1600 nm. Loading with transparent titania, maintains high transmittance in the visible with significant increase in the absorption in the UV and NIR ranges. Pt coated samples decrease transmittance across the UV, visible and NIR without changing the haze of the material. This can be expected since platinum has absorption across the spectrum and emphasizes the effect of the titania particles increase in the UV and NIR. For black-nickel plated samples, the transmittance greatly reduced due to the highly absorptive nature of the material. The haze for the black-nickel
plated colloids also greatly increased, due to the non-transparent, scattering behavior of the colloids.

**Figure 5.16** UV/Vis/NIR data for the base photoresist (NOA81, red), titania pyramid loaded NOA81 (TiO$_2$/NOA81, green), 4 facet Pt coated titania pyramids (PT TiO$_2$/NOA81, blue) and single face black-nickel plated titania pyramids (B-Ni/NOA81, black).

While the optical data shows the anticipated characterization, further studies on the angular dependence reflectance and haze were a target research goal. However, due to the high degree of scattering from the micron scale pyramids, the angular dependent measurements did not show any dominating trend. This finding showed that while the fabrication strategy and metallization options give rise to a broad range of target colloid structures, their utility is inevitably dictated by the particle design in terms of size and shape. The micron scale pyramids appear to be large enough to create a high degree of haze, but small enough to prevent the targeted angular dependent reflectance and absorption. Selecting larger feature sizes may decrease haze and increase the angular dependent reflectance, but masters of larger pyramids were inaccessible for this study.
5.4 Conclusions and future work

By controlling the layer stacks, direction of patterned features, and order of metallization and imprinting steps, a broad range of structures can be achieved with one set of materials. Each step is accessible for high throughput manufacture due to short process times, ease of fabrication and access to tooling. From the samples tested, it can be found that by tuning individual metal layers that the optical effect of the coating can be changed from highly transparent to dispersive to absorptive. The optical grade nanoparticle composite pyramids prevent a significant increase in haze and absorption in the visible, while black nickel provides control over the visible absorption. Future work on stamp lifetime and roll to roll manufacturing for large volume manufacture of custom colloidal structures will facilitate the use of these precise fabrication techniques on a larger scale potentially accessible by commercial markets.\textsuperscript{1,36}
Appendix

Stamp Materials Protection Through Fluorosurfactant Additives and iCVD

A6.1 Introduction

As explained in chapters 3 and 4, the selection of imprint material is crucial to the success of the final device for ease of fabrication but was well for optimal optical properties. However, some imprint materials can be damaging to the stamp as its reactivity within the resin may affect the stamp/resin interface. Titania is known to be a photooxidation catalyst, it is used in windows water and air filters in order to oxidize carbon sources, which can also kill bacteria.\textsuperscript{10,14,17,18} PDMS can be converted to silica with UV and is converted much more rapidly in the presence of titanium oxide. These two facts indicate that using a titania-based resin with a PDMS stamp over time will deteriorate the stamp by oxidizing the surface, change the modulus of the stamp and promote undesirable adhesion. Once the surface of the stamp is oxidized to silica, the inorganic binder in the imprint resin can readily covalently bind to the stamp and greatly increase the adhesion. Therefore, different types of oxidation barriers will likely need to be tested to get a significant increase in stamp lifetime, which will greatly increase manufacturability and throughput.

iCVD is a perfect process for depositing few nanometer films by polymerization direction on surface by vapor phase initiation. An iCVD film of a 5-15 nm perfluorinated polymer layer could be deposited directly above the fabricated nanopatterned stamp to improve stamp lifetime and reduce adhesion as seen as process flow 1 in Figure A6.1. One potential issue with depositing the perfluorinated layer onto the fabricated stamp is that any roughness or thickness in the iCVD film will change the dimensions of the final structure. Optimizing a thin film deposition with minimal roughness minimizes these concerns and ensures that the master dimensions are matched.
closely in the imprint. For this study, the nanopatterned PDMS surface will be modified after stamp fabrication in order to determine the effectiveness of a thin perfluorinated film in increasing the number of imprints per stamp, specifically for titania-based resin.

**Figure A6.1** Fluorination scheme for iCVD deposition onto the stamp fabricated from a slanted grating master.

### A6.2 Experimental Section

#### A6.2.1 iCVD deposition onto PDMS

In order to provide the nanopatterned PDMS substrate for iCVD depositions, a Si master of slanted gratings was fluorinated using the vapor phase process from chapter 4 and an XPDMS film stamp was cast and cured following the manufacturer’s specifications. After stamp release, the nanopatterned XPDMS stamp was used to deposit 10 nm of perfluorooctyl methacrylate or pentafluorophenyl methacyrlate by iCVD.

#### A6.2.2 Titania imprint process with uncoated stamps

As a secondary route to providing an oxidation barrier between the stamp and imprint materials, a fluorosurfactant is used in the imprint solution that is chosen to migrate to the surface of the stamp during the curing process. The selection process begins with a diblock polymer,
commonly utilized to target interfaces as a surfactant and short chain length to prevent any entanglement issues. Secondary considerations are solvent and material compatibility due to the titania composite imprint material and stamp’s nonpolar characteristic. Initially, Zonyl, an anionic fluorosurfactant previously available from Sigma Alderich, was chosen for these desired properties. The initial testing was quite successful even with 0.01 wt%. The features were generally more consistent and more challenging structures could be printed than compared to samples without the fluorosurfactant additive.

Once Zonyl was discontinued due to environmental hazards, the chosen drop in place substitute was Capstone FS66, which is a slightly larger molecular weight, which prevents accidental escape of PFAs into the atmosphere. With the same quantities as Zonyl, FS66 showed similar imprint success in comparison to without the additive.

To push the oxidation barrier further, a perfluorinated matrix is used to encase the nanocrystals in the composite. For this study, a perfluorinated diacrylate (Fluorolink MD700) and vertrel xF fluoro lubricant are used as the matrix and solvent, respectively. They are able to provide a strong enough matrix to replicate the pattern with high fidelity but reduce the refractive index sufficiently that the refractive index boost from the nanocrystals is negated.

**A6.2.3 Titania imprint process with iCVD coated stamps**

While the fluorosurfactant trials show promise for increasing stamp lifetime, they show no discernable increase in the success of imprints later in stamp lifetime trials. To further investigate the utility of fluorinated species to protect the stamp, the iCVD coated PDMS stamps were used to imprint into the titania nanocrystal composite including the fluorosurfactant. The large area replication success confirms the advantages of the technique while closer observation into the
aspect ratio of the resulting features is even more impressive. High aspect ratio features were imprinted up to 5 at a 45° angle, unseen in the research at this point.

6.3 iCVD Results and Discussion

There is an ideal balance between the solvent uptake into the stamp through the perfluorinated iCVD deposited barrier and reduced oxidation of PDMS to SiO₂ and solvent permeability. Therefore, imprinting trials with a patterned stamp are required to determine if curing is still feasible with less solvent uptake through the perfluorinated layer. A stamp lifetime trial with the PFM and uncoated stamps is conducted to compare imprint performance and lifetime. The stamp lifetime trial is conducted by doing 10 sequential imprints and determining to which imprint the stamp was successful, as assessed by the FEI Magellan 400 SEM. The hypothesis is that there is an ideal PFM thickness where the oxidation barrier properties are enhanced, and the solvent diffusion is sufficient to facilitate the cure.

For imprinting trials, a slanted grating master comprised of tilted and undercut lines is used. Tilted features are challenging to fabricate with brittle inorganic materials due to the adhesion and mechanical underpinning to the stamp in the undercut region. Most typically, the adhesion leads to chipping of the tip of the tilted line. A traditional stamp, which can provide one good large area imprint per stamp is compared to iCVD coated stamps and is shown to extend the number of good large area imprints to 3 or 4, a 300% increase in stamp lifetime. SEM images were taken of the stamp to determine if there are any deviation of the stamp features due to the iCVD deposition.

Some amount of roughness is observed on the stamp, which likely would be problematic for some high-end optics applications. Imprints from the stamp lifetime experiment show good
large area features and an increase in high-quality imprints per stamp from 1 to 3-4, depending on the acceptable defect density. The increase in stamp width and height due to the conformal deposition means the imprinted structure is significantly higher aspect ratio, which is typically more challenging. The antiadhesive and oxidatively resistant properties facilitate the fabrication of these more challenging features.

In order to confirm the presence and localization of the iCVD perfluoro layer, EDX was conducted on a cross section of the stamp, and the abundance of fluorine at the surface of the stamp features indicates the localization of the perfluorinated film to the surface. In this work, two techniques for utilizing iCVD for improvement of nanoimprint lithography stamps is demonstrated, formulation with a fluorosurfactant and iCVD coating of the stamp. In difficult applications with high aspect ratio and tilted features, the iCVD coatings improve stamp lifetime by up to 300%. While manual imprinting with these improved stamp coating is limited in its reproducibility, mechanization of the NIL process with iCVD stamps could prove out the stamp lifetimes accessible for large scale manufacturing.

A6.4 Conclusions and Future Work

While the results from this work are preliminary, through testing of iCVD deposited films with varying thickness can easily be tested on a variety of nano and micropatterns to assess the stamp lifetime increase. Additionally, performing iCVD directly into the fluorinated Si master and then subsequently depositing an iCVD interlayer, before casting of the XPDMS stamp would provide the highest level of feature fidelity due to the inclusion of the iCVD film thickness into the stamp bulk instead of into the fill space of the imprint material. This process, shown in Figure A6.2 would require optimization of the iCVD film and the interlayer film as the thickness...
of each is critical to the final stamp layer adhesion. This technique can also risk damage to the master due to an increased number of depositions step onto the master directly, therefore an “imprint master” approach is preferrable, where titania imprints of a structure can be fabricated and fluorinated for use as a master for iCVD film deposition optimization without risking the original master.

![Fluorination scheme for iCVD deposition pre stamp fabrication with a binary pillar master.](image)

**Figure A6.2** Fluorination scheme for iCVD deposition pre stamp fabrication with a binary pillar master.

### A7.1 National Innovation Corps Program

At the end of this thesis work, an NSF national I-Corps program was undergone to determine the product market fit of printed optics by NIL. Initially targeting metalenses for augmented reality, medical, telecom, laser and 3D sensing applications. The program entailed conducting 100 interviews in two months, writing weekly reports on the findings during interviews and final report outs. The cyclical fashion of the program enabled individuals to test new business hypothesis and validate or invalidate them with primary data from interviews. Weekly report outs to start-up experts and receiving their feedback helped drive the individuals in the program to think at the next level each week, building from minimum viable product
validation to customer channels and relations, and finally to key partners and costs. Learning to
construct a business model canvas and business plan helped researchers find the exact
application for their innovations and learn to ask the right questions. Building ecosystem maps of
the application landscape enable researchers to find entry points to decision makers at companies
and organizations that will likely be customers, influencers, or partners. Researchers infrequently
get the opportunity to learn this business focused skill set in the lab but adapting the analytical
skillset from lab to start up planning closes the loop between academia and industry.
Additionally, learning or confirming the major needs of the industry is a driving force to new
innovations.
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