NANOPATTERNING WITH PFPE ELASTOMERS: MATERIALS AND PHOTOVOLTAIC APPLICATIONS

by

Stuart Williams

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Approved By

Advisor: Professor Joseph M. DeSimone

Advisor: Professor Edward T. Samulski

Reader: Professor Sergei S. Sheiko

Reader: Professor John Papanikolas

Reader: Professor Wei You

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ABSTRACT

STUART WILLIAMS

Nanopatterning with PFPE elastomers: Materials and Photovoltaic Applications (Under the direction of Professors Joseph DeSimone and Edward Samulski)

Nanoscale fabrication is the foundation for emerging nanotechnology applications. This work describes the development and investigation of a soft lithography technique that utilizes perfluoropolyether (PFPE) elastomers for fabricating nanostructures from a variety of organic and inorganic materials. Inorganic oxides such as anatase phase TiO₂ are patterned from sol-gel routes. π -conjugated polymers are patterned into a myriad of shapes and sizes on the sub 500 nm length scale from both organic-based and aqueous solutions. Patterns are constructed with and without flash layers, over large areas, with varying aspect ratios, on different substrates, and from precursor materials that are not traditionally used in soft lithography applications.

Ordered bulk heterojunction solar cells are made from nanostructured titania and P3HT. Compared to a flat reference bilayer device, the short-circuit current was doubled upon nanostructuring, while the open-circuit voltage remained the same. The nanostructured device with the Z907 interfacial modification led to a power conversion efficiency of 0.6%. Photovoltaic devices comprised solely of organic materials were also fabricated, showing an increase in PV performance for nanopatterned devices compared to flat bilayer devices.

Several PFPE-based elastomers are explored for high resolution replica molding applications. The modulus of the elastomeric molds was varied using synthetic and additive approaches. High resolution nanofabrication techniques are reviewed, and the relationship between mold material properties and pattern fidelity is presented. Composite molds were used to form flexible molds out of stiff, high modulus materials. High arial density, sub-20 nm nanostructures are replicated using composite molds. Mold stability is experimentally investigated using sub-100 nm periodicity grating structures fabricated using e-beam lithography. It was observed that as the feature spacing decreased, high modulus PFPE-tetramethacrylate (TMA) composite molds were able to effectively replicate the nanograting structures without cracking or tear-out defects that typically occur with high modulus elastomers. In addition, the amount of fluorinated residue on a surface after contacting a PFPE molds is analyzed as a function of mold material and surface polarity. Suggestions for future directions of PFPE-based molding techniques are also presented.

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LIST OF ABBREVIATIONS AND SYMBOLS

a-PFPE	acryloxy perfluoropolyether
AFM	atomic force microscope (microscopy)
AM	air mass
BHJ	bulk heterojunction
CD	compact disc
DEAP	2,2-diethoxyacetophenone
DNA	deoxyribonucleic acid
DPN	dip-pen nanolithography
DRAM	dynamic random access memory
DRIE	deep reactive ion etch
DSSC	dye-sensitized solar cell
DVD	digital versatile disc
E	Young's modulus
EUV	extreme ultraviolet
FET	field effect transistor
FF	fill factor
FTO	fluorine tin oxide
γ	surface tension
h-PDMS	high-modulus PDMS
НСР	hexagonally close packed
η_{eff}	power conversion efficiency
hv-PDMS	photocurable PDMS

НОМО	highest occupied molecular orbital
HTM	hole transport material
IQE	internal quantum efficiency
ITO	indium tin oxide
\mathbf{J}_{sc}	short circuit current
LUMO	lowest unoccupied molecular orbital
М	molarity
M_{c}	molecular mass between crosslinks
μCΡ	microcontact printing
MDMO-PPV	poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]
μm	micrometer (micron)
MOSFET	metal oxide field effect transistor
μΤΜ	microtransfer molding
$M_{\rm w}$	molecular weight
NIL	nanoimprint lithography
NSL	nanosphere lithography
nTP	nanotransfer printing
ODT	octadecanethiol
OPV	organic photovoltaic
OTFT	organic field effect transistor
OWK	Owens-Wendt-Kaelbe
РЗНТ	poly(3-hexylthiophene)
рААО	porous anodized aluminum oxide

PANI	polyanaline
PC	photonic crystal
PCBM	phenyl C ₆₁ butyric acid methyl ester
PDMS	polydimethylsiloxane
PE	polyethylene
PEDOT:PSS	poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)
PEG	polyethylene glycol
PET	polyethylene terephthalate
PFPE	perfluoropolyether
PFPE-DMA	perfluoropolyether dimethacrylate
PFPE-TMA	perfluoropolyether tetramethacrylate
PMMA	polymethylmethacrylate
PMMS	poly[(3-mercaptopropyl)-methylsiloxane]
PnP	proximity field nanopatterning
PPV	poly(phenylenevinylene)
PRINT	particle (or pattern) replication in non-wetting templates
PS	polystyrene
PTEBS:Na ⁺	polythiophene poly[2-(3-thienyl)-ethoxy-4-butylsulfonate]
PTFE	polytetrafluoroethylene
PV	photovoltaic
REI	reactive ion etch
REM	replica molding
SAM	self-assembled monolayer

SAMIM	solvent assisted micromolding
SEM	scanning electron microscope (microscopy)
SERS	surface enhanced raman scattering
SFIL	step-and-flash imprint lithography
SPP	surface plasmon polariton
TDPTD	thermally deprotectable polythiophene derivative
TEM	transmission electron microscope (microscopy)
Tg	glass transition temperature
THF	tetrahydrofuran
ТМРТА	trimethylolpropyl triacrylate
UV	ultraviolet
V	Volt
V_{oc}	open circuit voltage
XRD	X-ray diffraction

Chapter 1

Literature Review and Introduction to Nanofabrication Techniques

1.1 Introduction to Nanofabrication: Application and Techniques

The fabrication and study of nanostructures $(1 \text{ nm} - 1 \mu\text{m})$ has been at the forefront of research in physics, materials science, chemistry, engineering, and biology for the past several decades. The field of "nanoscience" has grown due to the fact that interesting scientific phenomena occur on these length scales. Many materials and structures on the nanoscale exhibit properties that are unique from their bulk characteristics. Such examples of these properties and phenomena include quantized excitation,^{1,2} metal-insulator transitions,³ coulomb blockade,⁴ near-field optical behavior,^{5,6} single-electron tunneling,⁷ interaction of light with photonic band-gap crystals,⁸ and surface enhanced raman scattering (SERS).⁹ As nanofabrication techniques have become more common place, a large number of techniques have developed for a plethora of applications.

Historically, the primary application for materials nanofabrication has been microelectronics. Semiconductor technology helped spur the development of nanofabrication techniques and has had profound breakthroughs as a result. The miniaturization of functional devices to the nanoscale has led to better results for microchips – such as more components per chip, faster response, lower cost, lower power consumption, and higher performance.¹⁰⁻¹² The downward trend in feature size for semiconductor chips has been guided by the International Technology Roadmap for Semiconductors which is issued by the Semiconductor Industry Association, and predicts scaling of dynamic random access memory (DRAM) from a half-pitch of 52 nm in 2009 down to 8.9 nm in 2024.¹² Now that new nanofabrication techniques are widely available, new technologies and applications beyond microelectronics are being discovered across

all the major physical science disciplines; including medicine, biology, chemistry, physics, materials science, and engineering. In fact, reports on the processing, properties, and applications of nanomaterials appear rapidly, on a daily basis.

The ability to construct a nanoscale architectural design from various materials has opened up a number of technologies that rely on physical principles that are not available for macroscopic or microscopic structures. Revolutionary devices are being contructed that take advantage of nanofabrication techniques such as field effect (FETs).¹³⁻¹⁵ plasmonic nanoantennas.¹⁶ improved cells.¹⁷ solar transistors nanoelectromechanical systems,¹⁸ lithium-ion batteries,¹⁹ quantum dot lasers,²⁰ DNA nanoarrays,²¹ nanoparticles for drug delivery,²² medical devices, and chemical and biological sensors.²³ In all of these applications nanofabrication represents the biggest challenge and coincidentally the most opportunity for the realization of nanodevices, advancing current technologies, and discovering scientific phenomena.

1.2 Conventional Nanofabrication Techniques

Photolithography was one of the first nanofabrication techniques pioneered by the semiconductor industry, with the motivation of increasing the number of processors per unit area to make cheaper, faster, and more powerful computers. The development of the metal oxide semiconductor field effect transistor (MOSFET) spurred the use of photolithography for controlling the gate size in devices. As photolithography became more reliable, nanosized features started being fabricated with little error and high reproducibility.

Traditional, or conventional, forms of nanofabrication include photolithography and extensions of the technique that include projection photolithography (EUV or X-ray), immersion, electron-, and ion-beam lithography. Traditional nanofabrication techniques have been thoroughly developed and improved over a quarter century. All of the 'beam' lithography techniques have the same operational principal as shown schematically in Figure 1.1.²⁴ A material (typically a resist) is exposed to electromagnetic radiation in a spatially defined area which induces a chemical and physical change in the material and allows for the development of the material into relief structures. The relief structures are transferred to an underlying substrate material through etching. Projection lithography utilizes masks to determine which areas of a polymeric photoresist are exposed to radiation, or 'shot'. Most masks are made of quartz with a chrome pattern, which allows for light to pass through the transparent quartz area of the mask to effectively transfer the chrome pattern to the photoresist.

Scanning beam lithography (i.e. e-beam and ion-beam lithography) take advantage of extremely small beam sizes by directly 'writing' (or exposing) the area of a resist to the beam to construct a desired pattern. With direct write methods, or scanning probes and beams, a sharp tip or well defined beam of electromagnetic radiation induces local change in a resist or causes local deposition. These direct write methods are typically used to fabricate the costly masks used for photolithography instead of being used for actual device fabrication. The write-time for a scanning beam technique depends strongly upon the pattern density and feature seize. Patterning a dense array of sub-50 nm features over a 1 cm² area can take ca. 24 hrs with e-beam lithography. The long processing times restrict scanning beam methods to small areas and low feature density.



Figure 1.1 Schematic representation of photolithography and (left) pattern transfer to a substrate or (right) metal deposition onto the pattern structure (electroplating). (Reprinted with permission from reference 25. Copyright © 2005 American Chemical Society)

Traditional nanofabrication techniques still offer significant room for improvement from an engineering perspective, but there exists less chemical and materials innovation relative to new, unconventional forms of nanofabrication. Due to their thorough development, beam lithography techniques are commercially available and widely implemented in manufacturing processes. However, they are relatively costly processes that have low-throughputs and are restricted to mostly applications in the semiconductor industry. Additionally, harsh processing conditions that use corrosive etchants, high energy radiation, and high temperatures are employed that limit the ability to pattern biological and organic materials other than photoresists.

The limitations of conventional nanofabrication techniques motivated the exploration and growth of unconventional techniques. Unconventional nanofabrication

methods include both "top down" and "bottom up" approaches. A top down approach (such as photolithography) uses various lithography methods which utilize external forces or stimuli to form nanoscale patterns or structures in a material. Unconventional top-down approaches include molding,^{26,27} embossing,^{28,29} and printing.³⁰⁻³³ Bottom-up approaches rely on interactions between particles, molecules, or liquids to spontaneously form nanoscale patterns on a 2D or 3D scale. Unconventional bottom up approaches include self-assembly³⁴⁻³⁶ and scanning probe lithography.^{37,38}

1.3 Unconventional Nanofabrication Techniques

Unconventional techniques present exciting alternatives to current conventional lithographic techniques in manufacturing. Patterning of biological, organic, and organometallic materials, fabrication of nanostructures on non-planar surfaces, rapid prototyping of nanoscale features, and forming continuous nanopatterns over large areas are examples of opportunities and advantages that unconventional techniques have over conventional ones. Thus, unconventional techniques have the potential to provide a highthroughput, low-cost route to nanofabrication by utilizing processes such as reel-to-reel manufacturing. The simplicity of unconventional techniques for nanofabrication has allowed for widespread use and incorporation of nanofabrication into disciplines that were traditionally relegated to physics and electrical engineering. Because unconventional techniques are less developed, they are poised for more innovation.

1.3.1 Bottom Up Approaches: Self-Assembly

Self-assembly is the spontaneous organization of individual components into larger aggregates using covalent and non-covalent forces.³⁹ Self-assembly is a bottom up technology because it relies on cooperative interactions between molecules or particles to

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spontaneously form 2D or 3D structures. There are two types of self-assembly: templated and non-templated. Templated self-assembly is the most developed field, and uses external forces or pre-fabricated spatial constraints in conjunction with covalent forces acting on the individual components to form nanostructures. Due to the common use of pre-patterned structures formed using top down techniques to serve as the template, templated self-assembly is technically a 'partial' bottom up approach. Non-templated assembly relies solely on the covalent and non-covalent interactions between individual components to form larger structures.

Non-templated self-assembly is of interest due to the simplicity of the technique for forming nanostructures. The idea that a nanofabrication technique only has to rely on mixing two components is desirable for its potential efficiency. Some examples of nontemplated self-assembled materials include self-assembled monolayers (SAMs),⁴⁰ selfassembled block copolymers,^{41,42} and nanoparticles.^{43,44} Additional functional nanostructures fabricated using self-assembly include arrays of magnetic nanoparticles for magnetic data storage⁴⁵ and arrays of nanorods for birefringence.⁴⁶

Though spontaneous self-assembly is an attractive process, it is not a widely used technique for nanofabrication. Short-range defect free nanostructures are easily formed in many cases, but fabrication of nanostructures that display long-range order without a significant amount of defects is difficult. Due to the spontaneous nature of the assembly, the resulting nanostructures are determined by the energetics (covalent and non-covalent forces) of the system, instead of the architectural design required for a specific function or application. Material functionality is also an issue, as there are a limited number of components that will form self-assembled nanostructures. By adding an element into the pattern of self-assembled structure, it is possible to increase the self-assembly order. Surface topography,⁴⁷ electric and magnetic fields,^{48,49} and shear forces⁵⁰ have all been used to direct self-assembly. Spatial constraints, such as those formed by a microfluidic channel or the edge of droplet, are also used to direct assembly of materials into larger nanostructures.⁵¹ Templated self-assembly typically uses top down approaches to fabricating materials that drive bottom up assembly.⁵² Templated self-assembly is an alternative, or in some cases an extension, of non-templated self assembly that can be used to form desired patterns and nanostructures with both short and long range order.

Molecular templates are typically formed from organic materials and have been used as templates to mask the deposition of metals,⁵³ and guide the growth of nanoparticles,⁵⁴ and nanowires.⁵⁵ The non-functional molecular scaffold can then be removed to leave the desired functional nanostructure. Directed self-assembly of bock copolymers (schematic shown in Figure 1.2a) is also a very common technique used in the lithography community.⁵⁶⁻⁵⁹ Shown in Figure 1.2b are lamellae ternary Polystyrene-block-poly (methyl methacrylate) / polystyrene / poly (methyl methacrylate) (PS-*b*-PMMA/PS/PMMA) whose formation is guided by the underlying chemically patterned surface. The pre-patterned chemical surface acts as a guide to control the interfacial interactions of the block copolymer solution. Nealey *et al.* extended this concept using soft x-rays to chemically pattern surfaces over large areas and were able to quantify their results.^{56,60} This is a prime example of the ability of templated self-assembly to overcome the disadvantages of non-templated self-assembly in regards to long range

order, minimization of defects, and forming desired pattern structures that are not limited to the spontaneous assembly of components.



Figure 1.2 a) Schematic of the process used to fabricate chemically nanopatterned surfaces that direct the self-assembly of ternary blends in linear and bend geometries. (A) Photoresist was spin-coated onto a PS brush that was grafted to a silicon substrate and (B) patterned using advanced lithography to produce line and space features of period L_s . (C) Oxygen plasma etching was then used to chemically modify the exposed regions of the PS brush and to convert the topographic photoresist pattern into a chemical surface pattern. (D) The photoresist was removed by solvent treatment, and (E) a ternary block copolymer– homopolymer blend (PS-*b*-PMMA/PS/PMMA) was coated and annealed on the chemical surface pattern. b) Top-down SEM images of angled lamellae in the ternary PS-*b*-PMMA/PS/PMMA blend. The chemical surface patterns are fabricated with a L_s of 65 nm, and the lamellar domains of the block copolymer blend are self-assembled and registered are around bends with angles of 45° , 90° , and 135° . Patterns were formed over a 2 mm x 2 mm area. (Reprinted with permission from reference 60. Copyright © 2005, The American Association for the Advancement of Science)

Nanoparticles can also act as templates for self-assembly.⁶¹ By functionalizing spherical colloids with polyelectrolytes, the original nanoparticle can be removed yielding a stable, self-assembled polyelectrolyte spherical particle.⁶² In addition, this same templating can be done using metal depositions onto nanostructured surfaces, with subsequent removal of the nanostructure, yielding unique shapes and sizes of metal nanoparticles.⁶³ Multiple depositions can be employed to form multifunction particles that have been used for applications ranging from SERS⁶⁴ to anticancer drugs.⁶⁵

The field of self-assembled nanostructures is currently growing at a torrid pace, and new functional designs and applications are being developed using self-assembly as a nanofabrication technique. Self-assembly has tremendous potential as a nanofabrication technique considering the possibilities in forming structures in three dimensions, fabricating reconfigurable⁶⁶ or even reversible structures,⁶⁷ and the fact that some can undergo self-replication or self-repair.⁶⁸ Self-assembled structures are already present throughout the biological world, and act as an inspiration to the level complexity that can be achieved using this technique. However, due to the lack of control over spatial positioning, structure architecture, and material functionality, there is still a significant amount of work that needs to be done for self-assembled systems to be commercially viable alternatives to traditional nanofabrication techniques.

1.3.2 Dip Pen Nanolithography

Dip pen nanolithography (DPN) is a direct-write technique that uses a nanosized tip to deliver collections of molecules to specific areas on a surface. The discovery of DPN is unique from other scanning probe lithography methods because it is a constructive method used to deliver molecules or materials to a surface rather than a

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destructive method that relies on delivery of energy to a surface to remove or change a material. Some examples of destructive scanning probe techniques are anodic oxidation,⁶⁹ nanografting,⁷⁰ nanoelectrochemical patterning,⁷¹ and thermomechanical writing.⁷² DPN was first developed in 1999 by Mirkin and co-workers at Northwestern University.⁷³ They coated an AFM tip with an "ink", 1-octadecanethiol (ODT), and brought the tip into contact with a gold substrate. Water that condenses in the narrow gap between the tip and the substrate allows for the ODT molecules to transport through the water capillary and anchor themselves on the substrate through chemiabsorption (shown schematically in Figure 1.3A). Shown in Figure 1.3B, are lines of octadecylphosphonic acid on SiO₂ formed at varying write speeds. As the AFM tip moves faster, the lines become thinner. Mirkin and co-workers used DPN to pattern 30 nm lines of ODT on the gold surface.

DPN has been extended beyond the writing of alkanethiols on gold, to include many combinations of "inks" and substrates. Inks that have been used include various small molecules, metal ions, nanoparticles, polymers, oligonucleotides, peptides, and proteins.^{37,74} Substrates that have been used include gold, glass, quartz, silicon, gallium arsenide, and germanium.^{37,74,75} By applying thermal and electrostatic field control of the tip, DPN can be used as a spatio-controlled synthesizer for *in situ* building of quantum dots, nanowires, and carbon nanotubes on a surface.⁷⁶

The greatest limitation of patterning large areas using scanning probe techniques, such as DPN, is their serial nature. In 2000, Mirkin and coworkers first developed an eight pen nanoplotter that was used for parallel DPN.⁷⁷ This lead to the development of a 55,000 passive-pen array (shown schematically in Figure 1.3C), the highest density and

largest working scanning probe array ever fabricated.⁷⁸ The 55,0000 pen array was used to pattern features over large areas with sub-100nm control over shape and size, as shown in Figure 1.3D. It has been shown that DPN can be scaled to include an array with up to 1 million pens that occupy ~20 cm², which suggests that large-area nanofabrication via DPN is a possibility.⁷⁶ Huo et al. extended beyond arrays of tips mounted on individual cantilevers by developing a low-cost soft elastomer tip array for a technique called polymer pen lithography.⁷⁹



Figure 1.3 (A) Schematic representation of DPN showing the water meniscus that forms between the OTD coated AFM tip and Au substrate (Reproduced with permission from reference ⁷³. Copyright © 1999, The American Association for the Advancement of Science.) (B) Lines in octadecylphosphonic acid on a SiO₂ substrate. Lines were constructed at write speeds of 0.04, 0.16, and 0.64 μ m/s (left to write) which resulted in different thickness. (Reproduced with permission from reference 80. Copyright Copyright © 2006, American Chemical Society) (C) 3D drawing of massively parallel DPN with a passive, wire-free, 2D cantilever array and (D) optical micrograph of a representative region of the substrate in which approximately 55,000 duplicates were generated. Inset is a high resolution topographical AFM image of the representative replica. (Reproduced with permission from reference 78. Copyright © Wiley-VCH Verlag GmbH & Co. KGaA).

Though muti-pen arrays have been used on a research level scale, they have not been used to for a specific application. In order for these large through put methods consisting of multi-pen arrays to become a realization, a significant amount of engineering requirements that are application dependant must be met. New techniques need to be designed that allow for individually inking each pen within an array, and also independent control of each pen in the array, to form an 'active' array. As active arrays are further developed for DPN, sub 50-nm DNA array features for sequencing applications become a possibility. As DPN continues to undergo innovation improvements, the capabilities should allow for ability of researchers to study important phenomena and processes in the life sciences.

1.3.3 Top Down Approaches: Hard Pattern Transfer Elements

Techniques such as relief printing and injection molding use hard molds as a template to form patterns into monomer, prepolymer, or polymer substrates. Several commercial applications that utilize hard molds include patterning of compact discs (CDs), holographic gratings, diffraction gratings, digital versatile discs (DVDs), and plastic parts.⁸¹⁻⁸⁷ Developed as an alternative to photolithography, the use of hard molds was extended to forming nanoscale features in polymeric resists. As traditional lithographic techniques employ up to 40% of the cost of the semiconductor industry, ¹² engineers have sought to minimize the use of photopatterning polymeric resists by using a more mechanical approach to nanofabrication. The goal is to use traditional lithographic techniques to pattern a single master template, and from that template, reproduce the desired structures by either embossing or molding.
A number of different materials have been used as hard molds such as silicon, quartz, and various metals.³⁰ The most widely used materials have been silicon and quartz. The use of hard molds offers a number of advantages over traditional nanofabrication processes. The high modulus (> 50 GPa) molds retain nanoscale features with minimal local deformation.⁸⁸ A hard mold is also stable under high temperatures used to cross-link, melt, or cure most polymer precursors. Silicon and quartz are chemically inert to most polymeric precursors and materials; however, physical adhesion of material to the mold during release is an issue. To overcome this problem, many hard molds are treated with a low-surface energy organosilane monolayer to minimize adhesion of the mold to the patterned polymer.

The two most widely used techniques that utilize hard molds for nanofabrication are nanoimprint lithography (NIL) and step-and-flash imprint lithography (SFIL). Nanoimprint lithography uses silicon or metal molds to emboss patterns onto flat polymer precursors or films using high temperature and pressure. Step-and-flash imprint lithography (SFIL) uses quartz molds to form a pattern in a low-viscosity liquid prepolymer by photocuring through the optically transparent mold.

1.3.3.1 Nanoimprint Lithography

Imprint lithography techniques have developed over the past several decades into important processes for a wide variety of applications from biology to physics. Traditional NIL was first developed by Chou and co-workers utilizing silicon molds to imprint features with ultra-high resolution (as small as 10 nm) into polymer melts at high temperature and pressure.^{28,29} The process is composed of two steps, shown in Figure 1.4. First, a nanoscale topographically patterned silicon or silicon dioxide mold is pressed into

a thin polymer film under controlled temperature and pressure. Second, the system is allowed to cool and the mold is released from the polymer leaving a surface relief pattern, or thickness contrast, in the polymer film. Because the process requires heating the polymer above its glass transition temperature, NIL has been referred to as "hot embossing." For example, to pattern a poly(methyl methacrylate) (PMMA) resist, the system must be heated to 110 °C. After mold removal, a thin residual layer of polymer is left between the master-mold and the substrate onto which the polymer resist is patterned. The residual layer, or flash layer, acts to protect the mold from making direct contact with the underlying substrate and damaging the delicate nanoscale features on the mold surface. The formation of the flash layer is an energetically favorable process and cannot be removed during the imprinting of the resist. For most applications the flash layer is removed to complete the pattern definition. Typically this is accomplished by either an oxygen plasma-etch or a deep reactive ion etch (DRIE).



Figure 1.4 Schematic of the originally proposed NIL process (left). SEM image of a fabricated mold with a 10 nm diameter nanopost array (top right). SEM image of hole array imprinted in PMMA made by using the mold above (bottom right). (Reproduced from reference 89. Copyright © 1997 AVS)

NIL has quickly developed into an ultra-high resolution nanofabrication technique. Figure 1.3 shows 10 nm cylindrical pillars in a silicon mold, which was used to pattern 10 nm holes in a PMMA resist. Due to its simplicity and availability, coupled with the capability to pattern materials other than photochemically curable photoresist, NIL has been exploited for numerous applications. Electronic applications that utilize NIL include hybrid plastic electronics,⁹⁰ organic electronics,⁹¹ and nanoelectronic devices in silicon^{92,93} and gallium arsenide (GaAs).⁹⁴ Photonic applications include organic lasers,⁹⁵ nonlinear optical polymer nanostructures,⁹⁶ high resolution organic light-emitting diode (OLED) pixels,⁹⁷ diffractive optical elements,⁹⁸ and broadband polarizers. NIL has also been developed for biological applications such as protein patterning,^{99,100} pattern effects on cell culture,¹⁰¹ and DNA manipulation in nanofluidic channels.^{102,103}

Because NIL relies on the mechanical deformation of polymers for forming patterns, a new set of challenges and issues arise that were non-existent for traditional nanofabrication techniques. Mold lifetime and durability is one of the most important issues. In order for NIL to be an economically viable process, the mold must be able to last through a large number of imprinting cycles. Currently, nanoimprint molds require replacement after 50 cycles. The heating, cooling, and high pressure (50 - 130 bar) cycles applied during embossing cause molds to degrade as a result of stresses. In addition, the molds must have sufficiently low thermal expansion coefficient so that the delicate nano-sized features are not distorted during the thermal imprinting process. Another important issue is mold release. It is quite common for the resist material to adhere to the mold upon release. To mitigate these issues, the mold is often coated with a low surface energy coating or release agents are added to the resist. However, the lifetime of the coating is less than that of the mold, and often it needs to be re-applied. This can result in part of the low surface energy coating to become transferred onto the patterned nanostructures which can limit application performance.

The high viscosity of most polymer films has led to a number of nanofabrication challenges. There exists an optimal size and feature pattern density in NIL techniques. Patterning nano-scale objects is more facile than micrometer sized objects, due to the long process times required to fill large recesses in the mold. Changes in pattern density also create complications for NIL, as a mold with a range of feature sizes may result in pattern defects due to incomplete filling and uneven displacement of the embossed film.

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In addition, air trapped in cavities of the mold can result in incomplete filling. Flash layer uniformity is also an issue, which affects pattern transformation to the underlying substrate.

1.3.3.2 Step-and-Flash Imprint Lithography

Step-and-flash imprint lithography was first developed by Willson and co-workers utilizing transparent quartz molds to form patterns into photocurable polymer precursors.²⁶ As shown in Figure 1.5, SFIL uses a topographically patterned quartz mold that is pressed into a photochemically curable liquid precursor. The low-viscosity liquid, commonly comprised of a low molecular weight polymer and photoinitiator, easily fills the nanocavities of the mold upon contact. The liquid is solidified or hardened by exposure to light through the mold. The mold is then released, leaving a surface relief pattern with features inverted relative to the mold template.

SFIL avoids incomplete filling by using a low viscosity liquid, which is easily displaced without the use of high temperature and pressure. Additionally, pattern density issues that cause problems in NIL are not present in SFIL.^{104,105} Because SFIL is performed at room temperature (~ 22°C) and low applied pressure (< 1 lb/in.²), there are no distortions due to thermal expansion. Layer-to-layer alignment, printing onto brittle structures, patterning curved surfaces, and patterning topographies with multiple depths on a single step are also advantageous that SFIL has over its NIL counterparts.^{26,106}



Figure 1.5 Process schematic for step and flash imprint lithography. (Reprinted with permission from reference 107. Copyright © 2005 SPIE)

The bulk of current research for SFIL has focused on semiconductor nanofabrication, which has led to dramatic improvements in mold-template fabrication, defect analysis, and resist materials. Patterns with feature sizes down to 20 nm, shown in Figure 1.6 have been patterned using SFIL.¹⁰⁷ Alignment accuracies as high as ± 10 nm (3 σ) have also been reported. Though the need for a mold release layer is present in SFIL, recent developments have reported the ability to undergo 1500 patterning cycles without having to replace the functional layer.¹⁰⁸



Figure 1.6 Features in resist produced by SFIL. Dense 50 nm lines (top left). 20 nm semi-isolated lines (top right). Printed 60 nm posts (bottom left). 40-nm line pattern printed with template used over 1500 times (bottom right). (Reprinted with permission from reference 107. Copyright © 2005.SPIE)

Though SFIL is an impressive high resolution nanofabrication technique, a number of challenges exists, such as the previously mentioned flash layer issues and need for release layer functionalization. Expensive machinery is required to ensure that the mold and substrate are extremely flat and parallel. A slight non-uniformity in moldsubstrate alignment can result in incomplete filling and an uneven flash layer. In order for SFIL nanofabrication techniques to become useful for additional applications, the development of new precursors will be needed. Precursors currently available do not include materials with functionality appropriate for optoelectronic and ferromagnetic applications.

1.3.4 Top Down Approaches: Soft Pattern Transfer Elements

The past few decades have witnessed the emergence of soft lithography as an important tool for low cost pattern replication on the micron and nanometer scales.³¹ The

term "soft lithography" refers to the soft elastomeric mold, or stamp, that is formed by curing a liquid polymer precursor against a topographically patterned master. Like its hard material counterparts, soft lithography was originally developed as an alternative to photolithography for the manufacture of integrated circuits and other devices with sub-50 nm feature sizes. Now a wide variety of applications are being pioneered by nanofabrication techniques that fall under the umbrella of soft lithography. Some of these soft lithographic methods are depicted in Figure 1.7 and include replica molding (REM), microcontact printing (μ CP),³² nanotransfer printing (nTP),¹⁰⁹ proximity field nanopatterning (PnP),^{110,111} and solvent assisted micromolding (SAMIM).³² Additionally, a technique called near-field phase-shift lithography was developed that utilizes the surface relief pattern of an elastomeric mold to form nanopatterns using conventional photolithography.¹¹² All of these soft lithography techniques use a patterned elastomer as a mold, stamp, or mask to generate or transfer a pattern.



Figure 1.7 Schematic representation of various soft lithographic methods utilizing elastomeric molds. (Reprinted with permission from reference 31. Copyright © 1999 American Chemical Society)

The field of soft lithography has traditionally been dominated by the elastomer poly(dimethylsiloxane) (PDMS).^{32,113} PDMS is an attractive material for several reasons;

(i) it has a flexible backbone that allows for the accurate molding and patterning of various 2D and 3D shapes, (ii) it has a low Young's modulus and low surface energy that allow for conformal contact of the mold to flat surfaces without externally applied pressures, (iii) it is a relatively tough material with a high elongation at break (> 150%) that allows for significant deformation before failure during patterning conditions, and (iv) it is commercially available in inexpensive kits from Dow Corning (Sylgard 184) that enable the material to be used in low-cost academic and research and development environments. PDMS molds have been used to pattern 2-dimensional as well as 3-dimensional structures,²⁵ with resolutions approaching the molecular scale,¹¹⁴ and are capable of patterning on both flat and curved surfaces.³²

Despite the advantage of PDMS for use in soft lithography, the most commonly used form of PDMS (Sylgard 184) has been shown to suffer from serious drawbacks. It swells in common organic solvents, and is known to leave cyclic silicone derivatives on surfaces being molded or patterned.¹¹⁵ This becomes a serious problem when trying to pattern certain biological materials or for the fabrication of functional nanostructures with controlled surfaces. Its low modulus is a detriment for patterning high-aspect ratio nanostructures as the nanostructures will collapse, merge, or buckle. Furthermore, the high thermal expansion coefficient (260 μ m/°C) and the thermal curing process can result in distortions during nanofabrication processes. In order to overcome some of these issues, a number of materials have been developed to expand the use of soft lithography. These materials and techniques are discussed in detail in Chapter 4.

1.3.5 Pattern Replication In Non-wetting Templates (PRINT)

In 2004, Rolland *et al.* exploited the excellent solvent resistance and inherent release properties of highly fluorinated perfluoropolyether (PFPE) elastomers as an exceptional molding material.^{116,117} The unique range of material properties of PFPE-based elastomers of high chemical resistance, extremely low surface energy, high gas permeability, high solvent resistance, high elastic recovery and good mechanical strength, all translate into the ability of PFPEs to mold most organic and aqueous liquid precursors to generate useful materials in the form of isolated particles, arrays of particles, and arrays of patterned features for a number of applications in both nanomedicine and materials science.

Embossing is the process of creating a three-dimensional image or design in paper and in ductile materials. It is typically accomplished with a combination of heat and pressure. Unlike embossing, PFPE-based molding opens up unique approaches that exploit wetting, partial wetting, and non-wetting phenomena instead of relying on heat and pressure associated with traditional embossing approaches. As a result of the very low surface energy and high gas permeability of PFPE-based materials, it is possible to mold materials by exploiting the ability to "dead end" fill recessed cavities in PFPE molds with a wide range of curable organic liquid precursors. Depending on the exact details of how the filling process is completed (Figure 1.8), including the exact nature of the precursor to be molded, we can uniquely fabricate isolated particles, arrays of particles and arrays of patterned features using a combination of cavity filling and free meniscus coating concepts. We have reported the fabrication of features ranging in size from two nm to hundreds of microns, and have demonstrated that we are able to accurately mold and replicate nanometer-scale features with a resolution of 0.4 nm.¹¹⁸

In addition to the unprecedented resolution enabled by the use of PFPE-based materials in molding processes, we find that we can fill recessed cavities within the PFPE molds with most organic and aqueous liquids without wetting the land area between the cavities (Figure 1.8). As such, once the liquid contained in the cavities is solidified, discrete objects in the mold can be achieved without the formation of the ubiquitous "flash" or "scum" layer. The flash layer is common to traditional embossing or soft lithography techniques where applied forces are used.^{22,116,117,119} With PFPE-based molds, we can fabricate harvestable, flash-free objects, or particles using a process called PRINTTM (Particle [or Pattern] Replication In Non-wetting Templates).²²The PRINT process begins with the formation of a master template, typically an etched silicon wafer formed using advanced lithographic techniques (Figure 1.8a), which is coated with a photocurable liquid PFPE resin that is evenly distributed across the surface of the master template. Once the liquid fluoropolymer has completely wet the master template, it is photochemically crosslinked and subsequently peeled away to generate a precise mold having nanoscale cavities (Figure 1.8b). For the fabrication of 2-dimensional arrays of particles or free particles, the PFPE mold is filled with an appropriate liquid via capillary filling without wetting the land area around the cavities (Figure 1.8c). The liquid in the mold cavities is then converted to a solid using a wide range of methods including curing chemistries, evaporation, lyophlization, or liquid to solid phase transitions (Figure 1.8e, e`). The resultant particles can be removed from the mold and transferred to another surface to generate a 2-dimensional array or to yield free particles (Figure 1.8f,f`,g).



Figure 1.8 Schematic illustration of the PRINT process and traditional embossing processes: (a) silicon master template; (b) mold release from master template; (c) mold filling via capillary fill with countersheet having a higher surface energy than the PFPE mold; depending on the exact nature of the liquid to be molded and the details of the process, (d) one can fill the cavities only and not wet the land area around the cavities or (d') one can fill the cavities and have a thin layer of liquid on the land area around the cavities. The thickness of the layer of connecting flash layer liquid is determined from the principles associated with free meniscus coating processes with the resulting (e, e') pattern transfer to substrate, (f, f') mold release from array of isolated features, and (g) dissolution of the harvesting film to yield free particles. As an alternative to the PRINT process, one can use PFPEs using traditional embossing processes where pressure and heat are applied (h, i) to form an embossed film (j) after the mold is removed. (Reprinted with permission from reference 120. Copyright © 2009, American Chemical Society)

The PRINT process is unique over the imprint lithography techniques promulgated by Whitesides *et al.*³¹⁻³³ in that PRINT uses elastomeric fluoropolymers instead of silicones which results in three important distinctions: i) perfluoropolyether elastomers have a lower surface energy which enables the selective filling of nanoscale cavities in the mold with almost any organic liquid *without* wetting the land area around the cavities which enables distinct objects or particles to be formed even at the micro-and nanoscale; ii) organic liquids (such as hexanes, ethyl ether, toluene, acetone, dichloromethane) do not swell fluoropolymers like they do silicones, allowing for the fabrication of a wide range of organic particles with desired attributes (surface chemistries, degradation characteristics, deformability) (Figure 1.9); and iii) the TeflonTM-like characteristics of the fluoropolymer mold allows the resultant organic particles to be easily harvested or removed from the mold.



Figure 1.9 PRINT particles varying in size, shape, surface chemistry and deformability. The particle composition for all of these particles was approximately the same and included polyethyleneglycol (PEG) (bulk of the matrix), a cross-linker, and a linker group for conjugation of stabilizing groups (such as PEG) or targeting ligands (such as peptides, antibodies, etc). A) Scanning Electron Micrograph (SEM) of cubic-shaped particles with a cube side length = $2 \mu m$; B) SEM of cylindrical nanoparticles having diameter = 110nm and height = 35 nm; C) SEM of cylindrical nanoparticles having diameter = 200 nmand height = 200 nm; D) SEM of rod-like PRINT particles having diameter = 100 nm, height = 300 nm; E) SEM of micron-scale "boomerang" particles containing 15 wt.% magnetic resonance contrast agent, useful for inhalation studies; F) Cylindrical 7 (dia.) x 14 (h) µm particles containing a covalently attached red fluorophore that have been functionalized on one face with a generic linker group (green fluorophore) that will allow the conjugation of targeting peptides, antibodies and aptamers region-specifically onto the particle probes; G) and H) Particles for mechano-biology studies having approximately the same dimensions as red blood cells (cylinders with a diameter = $7 \mu m$ and a height of 1.7 µm made from (G) a non-deformable, highly cross-linked hydrogel; and (H) lightly cross-linked, deformable hydrogel. (Reprinted with permission from reference 120. Copyright © 2009, American Chemical Society)

1.4 Objectives and Overview

Nanoscience and nanotechnologies show promise to revolutionize many disciplines, technologies, and industries. Some nanotechnologies are already being implemented that have made a tremendous impact on the technological world. At the heart of these technologies is nanofabrication: the ability to design and construct a myriad of materials on the nanoscale with specific shape, size, and functions. In this work, we seek to further develop and investigate the PRINT technology for fabricating nanostructures out of a wide variety of both organic and inorganic materials, with a specific drive toward photovoltaic applications. Additionally, the fundamentals of nanopatterning using PFPE-based molds are investigated with some suggestions for future directions of nanofabrication and PRINT technology.

Conventional forms of nanofabrication were developed from the microelectronics industry, specifically for increasing number of transistors on a microchip; resulting in cheaper, smaller, more powerful computers. Due to their development for microelectronics applications, conventional nanofabrication techniques have traditionally been relegated to disciplines such as physics and electrical engineering. Photolithography (and extensions thereof) is the primary conventional nanofabrication technique, and requires flat substrates, expensive machinery, and ultra-clean environments.

Non-conventional techniques of nanofabrication have been developed over the last several decades to have an impact on a wide variety of disciplines such as chemistry, materials science, and biology. An extensive variety of engineering techniques and materials have been developed to allow nanofabrication for an array of applications. These techniques include self-assembly, nanoimprint lithography, step-and-flash imprint lithography, and soft lithography.

Self-assembly provides one of the simplest nanofabrication routes. Nanostructures are formed as a result of covalent and non-covalent interactions between components. There are two types of self-assembly, templated and non-templated. Templated methods rely on the use of external forces to control self-assembly, while nontemplated self-assembly does not. Typically templated self-assembly uses top down methods to form the template, thus 'templated self-assembly' is often thought of as a

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merging of "top-down" and "bottom-up" techniques. The integration of top down and bottom up assembly is best exemplified in block copolymer lithography. Immiscible block copolymers self-assemble into ordered morphologies on the nanoscale whose size and structure is determined by the volume fraction and processing conditions. One of the main applications for block copolymer lithography is data storage, which requires extremely high arial density nanoscale features over large areas. Block copolymer lithography and other high resolution nanofabrication techniques will be discussed in more detail in Chapter 4.

Nanoimprint lithography uses hard (typically silicon) masters to emboss polymers, biologics, and other organic materials into nanopatterns using applied heat and pressure. NIL is an extremely high resolution technique, and has extended the use of nanofabrication for other applications. The drawbacks to NIL include the ability to vary pattern density on the same substrate, incomplete filling for certain materials, issues with mold lifetimes, and the expensive tools necessary to keep the mold and substrate aligned under high pressures and temperatures. As an alternative to NIL, step-and-flash imprint lithography, SFIL, was developed for patterning low-viscosity photocurable resists. SFIL has shown the ability to pattern down to 20 nm lines, with a high degree of resolution and alignment. Since SFIL relies on molding materials (as opposed to embossing) at ambient temperatures and pressures, there are no lifetime, thermal expansion, or nanostructure stability (at high pressure) issues. As such, mold lifetimes in SFIL are much longer than NIL. The drawbacks to SFIL include the need to have the mold and substrate ultraflat, and the inability to pattern a variety of materials for non-electronic based applications.

Soft lithography was pioneered by Whitesides, and typically uses a patterned silicone based elastomer (Sylgard 184) for nanofabrication. Due to the elastomeric nature of the molds, a variety of techniques have been developed for nanofabrication using nanostructured PDMS based molds. These methods have allowed for patterning numerous materials, and have led to a lower cost barrier to nanofabrication. Though it is an inexpensive and ideal material for soft lithography there remain still many issues that plague the development of PDMS for commercial applications.

PFPEs were developed as an improved alternative to PDMS as a mold material for soft lithography. Due to the unique properties of PFPE-based molds, new nanofabrication technologies became available that allow for the construction of not only nanopatterns, but also isolated nanoparticles. The PRINT technology utilizes PFPEbased elastomers, and opens up the ability to pattern materials for applications ranging from photovoltaics to drug delivery. In this work, we utilize PFPE molds for patterning inorganic oxide and semiconducting polymeric materials for photovoltaic applications, and look into the fundamentals of nanofabrication using the PRINT technology.

This dissertation consists of five chapters. This chapter has given an introduction to nanofabrication techniques and their applications as well as a brief overview of current non-conventional nanofabrication methods. Chapter 2 describes the use of PRINT technology for forming nanopatterns in inorganic oxides and semiconducting polymers. These patterns were formed using a number of techniques that afforded a variety of nanostructured shapes and sizes. Photovoltaic applications of nanostructures formed using the PRINT technology are discussed in Chapter 3. Comparisons are made between nanopatterned solar cells and flat bilayer solar cells. Chapter 4 discusses the more fundamental aspects of nanopatterning with PFPE-based elastomers and blends. High resolution nanofabrication techniques are reviewed, and the relationship between mold material properties and pattern fidelity is presented. High arial density nanostructures are replicated, and mold stability for closely spaced, high aspect ratio nanostructures is discussed. Additionally, the issue of fluorinated residues left from PFPE molds is analyzed and trends are displayed as a function of mold material and surface energy. Recommendations for future directions are presented in Chapter 5.

1.5 References

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Chapter 2

Patterning of Inorganic Oxides and π -congugated Polymers via PRINT

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2.1 Introduction

As summarized in Chapter 1, the replication of nanometer sized features is a challenging materials problem. In this chapter, the low surface energy, high gas permeability, and chemical inertness of crosslinked PFPE-based fluoroelastomer materials are showcased for the replication of nanometer sized features. Additionally, we illustrate the use of aggressive chemistry techniques during the PRINT processes; enabling the formation of uniquely patterned, sub-500 nm-sized inorganic oxide and semiconducting polymers. These materials have potential applications in photovoltaics, super capacitors, biological sensors and electrodes, and various other electronic and optical devices.¹⁻¹¹

A range of oxides including titanium dioxide (TiO₂), tin oxide (SnO₂), zinc oxide (ZnO), tin-doped indium oxide (ITO), and barium titanate (BaTiO₃) were formed into arrays with control over size, shape, and composition, both with and without an interconnecting flash layer. Reports in the literature detail the patterning of sol–gel-derived inorganic oxides using traditional soft-lithography techniques.¹²⁻¹⁵ Most notable have been the research efforts of Whitesides and co-workers, who employed PDMS molds and liquid sol–gel precursors in order to replicate surface patterns (down to 1mm).¹⁶ There have also been reports of features with sizes smaller than 500 nm; these resulted from a significant volume reduction of the sol–gels after calcinations using micrometer-sized elastomeric molds.^{17,18}

In attempts to replicate sub-100 nm features, we fabricated porous anodized aluminum oxide (pAAO) to serve as master templates. Both ordered and non-ordered pores in Al_2O_3 were synthesized. It is well known that an ordered hexagonally close

packed (HCP) array of pores is formed by anodizing aluminum under appropriate conditions.¹⁹⁻²⁵ Using a standard two step procedure the pore diameter, depth, and periodicity can be tailored altered.²² Using an electrochemical growth process, pores can be constructed that are on the order of 20-140 nm in diameter with aspect ratios as high as $1400.^{21}$ In this work, we report the fabrication of low aspect ratio, 20 nm diameter pores in pAAO for replication in TiO₂ using PRINT. Though the pAAO membranes can be replicated in the TiO₂ xerogel, there are significant challenges that occur for crystalline TiO₂ replicated from large area pAAO membranes.

In the last section of this chapter, the application of the PRINT process is shown to include the patterning of 200 nm cylindrical features of semiconducting polymeric materials on various surfaces. Polymers that are π -conjugated have been the focus of intense synthetic and engineering research for their (i) tunable optical and electronic properties (ii) mechanical flexibility (iii) ability to be solution processed and (iv) relatively low cost. These properties have led to the use of semiconducting polymeric materials instead of inorganic materials as the active component in many optoelectronic devices such as polymer light emitting diodes,^{26,27} field effect transistors,²⁸ nanowires,¹¹ and photovoltaic devices.²⁹ Many of these device architectures require the active polymer layer to be constructed in a desired morphology, or processed in a specific pattern. Traditional nanofabrication techniques are not amenable to processing most conjugated polymers, though there have been several promising reports of materials such as pentacene,^{30,31} polyanaline (PANI),⁸ polythiophenes,³² and polyphenylenevinylene (PPV) derivatives^{33,34} using photolithographic techniques. However, there exists many drawbacks to using these processes such as the use of aggressive chemistries for

development and exposure of nanopatterns, difficulty in resolution and alignment of features on rough, non-planar plastic substrates, and challenges associated with fabricating large-area patterns in an economically viable fashion.

There have been numerous reports in the literature of using soft lithography to form micron and nanometer patterns in organic polymers for organic electronic and optoelectronic applications. Whitesides and co-workers first reported the use of micromolding in capillaries (MIMIC) to pattern features ranging from 50 µm to 350 nm in PANI,³⁵ and more recently used a technique called nanoskiving for forming laterally ordered bulk heterojunctions.³⁶ MIMIC has also been used to pattern nanodots out of conducting polymers,³⁷ and thin-film transfer techniques have been utilized for fabricating all-polymer photovoltaic devices.³⁸ As the requirement for device performance increases, there is a growing demand for controlling the device architecture for various electro-active polymers.

Herein we showcase the use of PRINT for patterning several different π conjugated polymers that are used in various optoelectronic devices. We are able to fabricate ordered arrays of 150 nm diameter x 500 nm height cylindrical structures over large areas. We successfully demonstrate that the PRINT process can be used with aqueous-based solutions and organic based solutions for nanofabrication of polymers with drastically different solubility parameters. In addition, we are able to extend from fabricating 2D nanostructures on a surface to fabricating 3D particles on the micron length scale.

2.2 Experimental

2.2.1 Materials and Characterization Techniques

Unless otherwise stated, all materials were purchased from Aldrich and used as received. All metal oxides were characterized with an x-ray diffractometer (XRD, Rigaku) using Cu K α radiation. SEM micrographs were obtained with either a Hitachi S-4700 instrument or a FEI Helios 600 NanoLab Dual Beam System.

2.2.2 Master Template Fabrication

200 nm diameter cylinders: The 200 nm cylindrical features, and any other features with larger dimensions, were fabricated using standard projection photolithography techniques. pAAO templates: High purity (99.99%) aluminum foil was first electrochemically polished in a 70% perchloric acid ethanol mixture with a volume ratio of 3:7 at 60 V. The polished aluminum was placed in a Teflon[™] cell enclosed in an ice bath to regulate the temperature. The cell was designed such that one side of the aluminum is in contact with the copper plate serving as the anode and the other side is exposed to the electrolyte solution with a platinum wire serving as the cathode. Using a 0.3 M oxalic acid solution as the electrolyte, the first anodization was carried out over 3 hours with the temperature regulated between 5 and 10 °C. The solution was vigorously stirred to keep an equilibrium temperature on the surface of the foil; otherwise local hotspots would oxidize through the film and cause disorder in the bottoms of the growing pores. After oxidation, the Al₂O₃ layer was removed by etching the Al₂O₃ in a 1.8 wt% chromic acid and 6 wt% phosphoric acid solution with a volume ratio of 2:8 at 60 °C for 40 min. After rinsing with ethanol and water, the second anodization was carried out using the same conditions as the first for a controlled amount of time in order to control the pore depth. The pore diameter could be widened by immersing the sample in a 5 wt% phosphoric acid solution for 30 minutes.

2.2.3 Sol-gel Synthesis

To make titania sol 1, titanium butoxide (Ti(OBu)₄; 10.0 g, 29.4 mmol) was combined with acetylacetone (6.80 g, 68.0 mmol). After 15 minutes of stirring, 2propanol (8.0 mL) was added to the solution. Glacial acetic acid (0.252 g, 4.19 mmol) was added dropwise to the stirring solution. The sol was stirred for 1 h and filtered with a 0.45 μ m filter before use. To make titania sol 2, the same procedures were followed with different molar ratios of Ti(OBu)₄ (9.0 g, 26.4 mmol), acetylacetone (0.262 g, 2.62 mmol), 2-propanol (0.20 mL), and glacial acetic acid (0.079 g, 1.31 mmol). To convert TiO₂ into the anatase form, samples were heated to 450 °C at a rate of 5 °C per minute and held at 450 °C for 30 minutes. To prepare the SnO₂ sol, SnCl₂•2H₂0 (3.82 g, 16.9 mmol) was dissolved in anhydrous ethanol (37.5 mL). This solution was refluxed at 80 °C for 2 h and allowed to cool to room temperature and filtered with a 0.45µm filter before use. In order to obtain crystalline SnO₂, samples were heated to 450 °C at a rate of 10 °C per min and held at 450 °C for 30 minutes. To make the ZnO sol, zinc acetate dihydrate (2.20 g, 10.0 mmol) was dissolved in 2-propanol (10 mL). Diethanolamine (1.05 g, 10.0 mmol) was added rapidly to the stirring solution. The solution was heated to 50 °C and after 10 minutes, DI water (0.09 mL) was added dropwise. The solution was allowed to cool to room temperature and then was filtered with a 0.45µm filter before use. In order to obtain crystalline ZnO, samples were heated to 500 °C at a rate of 10 °C per minute and held at 500°C for 1 h. To prepare the sol precursor of ITO, indium nitrate pentahydrate (2.05 g, 5.24 mmol), tin chloride pentathydrate (0.15 g, 0.428 mmol), acetylacetone (3.16 g, 31.6 mmol), and water (0.009 mL) were combined in one vial and stirred at 50°C for 2 h. In another vial, benzoylacetone (0.851 g, 5.25 mmol) and 2methoxyethanol (20.7 mL) were combined and allowed to stir at room temperature for 2 h. The solutions in the two vials were combined and allowed to stir at room temperature for at least 8 h before used. To convert ITO to the crystalline form, samples where heated to 600 °C at a rate of 10 °C per minute and held at 600 °C for 1 h. To make the BaTiO₃ sol, a 42 wt.% barium acetate solution in glacial acetic acid was prepared by dissolving barium acetate (0.382 g, 1.50 mmol) at 85 °C. The sample was then cooled to 50 °C and titanium(IV) isopropoxide (0.417 g, 1.47 mmol) was added. The solution was diluted with 2-methoxyethanol (0.1 mL) and filtered through a 0.45 µm PTFE filter. In order to obtain crystalline BaTiO₃, samples were heated to 700 °C at a rate of 10 °C per minute and held at 700°C for 1 h.

2.3 Results and Discussion

2.3.1 Patterning of Inorganic Oxides

A schematic representation of the PRINT process used to pattern inorganic oxides from sol-gel precursors is illustrated in Figure 2.1 (a – e). A silicon master template with the desired dimensions is first fabricated using standard lithographic techniques. A liquid PFPE precursor solution comprising 1 kg mol⁻¹ PFPE α , Ω -functionalized dimethacrylate and 2,2-diethoxyacetophenone is then poured over the nano-patterned master template. The PFPE precursor is then photochemically crosslinked to provide an elastomeric mold of the master template. In order to obtain an array of isolated features (as shown in Figure 2.1, c₁-e₁), the mold cavities are filled with a liquid sol by taking advantage of capillary fill processes. The sol is dropped onto the mold and a high surface energy poly(ethylene) sheet is laminated to the mold and then slowly peeled away at a controlled rate to remove excess sol from the mold. The filled mold is then placed face-down on a substrate, constant pressure is applied to the mold, and the entire assembly is held at an elevated temperature in order to undergo the sol-gel transition via solvent removal, which is assisted by the gas permeable mold.¹⁷ To obtain an embossed film (as shown in Figure 2.1, c_2 - e_2), the liquid sol is dropcast onto the substrate and the mold is pressed down and held at constant pressure. The sample is then held at an elevated temperature in order to undergo the sol-gel transition. In both situations, the low-surface energy PFPE mold is peeled off the substrate leaving either isolated xerogel features or an embossed xerogel film as shown.

Once in the xerogel state, the substrate is calcined to form the desired crystalline phases. In the case of patterning TiO_2 , the anatase phase is preferred due to its potential use in applications involving photocatalysis.³⁹



Figure 2.1 Schematic illustration of the PRINT process: (a) silicon master template; (b) mold release from master template; (c₁) mold filling via capillary fill with poly(ethylene) sheet; (d₁) pattern transfer to substrate at elevated temperature and pressure; (e₁) mold release from array of isolated features; (c₂) embossing a liquid precursor; (d₂) pattern transfer to substrate at elevated temperature; (e₁) mold release from an embossed film.

Figure 2.2 is a SEM micrograph of an array of isolated anatase titania features

that have been patterned on a glass substrate using the procedures outlined in Figure 2.1,

 $a - e_1$. In order to demonstrate the formation of an isolated array of features, a doctor's

blade has been used to scrape the surface of the substrate.



Figure 2.2 SEM micrograph of an array of isolated anatase TiO_2 features. The pattern has been scraped with a doctors blade to demonstrate the lack of an interconnecting flash layer between features.

Figure 2.3 is a SEM micrograph of an embossed array of patterned anatase TiO_2 replicated from a silicon master template consisting of a hexagonally-patterned array of cylindrical posts each 200 nm in diameter and 200 nm in height. Transmission electron microscopy (TEM) shows that the resulting anatase morphology consists of crystallites that are approximately 10 nm in dimension.



Figure 2.3 SEM micrograph of anatase TiO_2 features on glass replicated from a silicon master with 200 nm diameter cylinders that are 200 nm in height.

In order to obtain these patterned titania features, traditional sol-gel chemistry techniques have been employed. To prepare a stable TiO_2 sol, the inorganic precursor titanium tetrakis(*n*-butoxide) $Ti(OCH_2CH_2CH_2CH_3)_4$ was chelated with acetylacetone.
This solution was diluted with 2-propanol before adding acetic acid as a catalyst. Upon solvent removal at 110°C, a xerogel was formed. This amorphous solid was calcined at 450° C to obtain the anatase form of crystalline TiO₂.³⁹ The characteristic powder X-ray diffraction (XRD) pattern of the bulk powder harvested after calcination of sol **1** (see Table 2.1) is shown in Figure 2.4



Figure 2.4 XRD spectrum for TiO₂. Sample from bulk sol-gel powder.

SEM micrographs of patterned substrates are shown in Figure 2.5A and 2.5B before calcination and in 2.6C and 2.6D after calcination. The width and height of the xerogel features closely approximate the mold size, indicating good filling of the mold and a porous, amorphous network. After calcination, both the width and height of the features decrease; however, shrinkage along the z-axis is more significant. This anisotropic volume loss has been observed in other work.^{12,13}



Figure 2.5 Array of isolated titania features on an ITO coated glass slide from a 200 x 200 nm mold using sol 1. (A) and (B) in the xerogel and (C) and (D) after calcination to form the anatase titania patterns.

Shrinkage of titania features after calcination is expected based on the low weight percent of solids in the sol formulation. Through modification of the sol recipe however, this volume loss can be minimized. Recipes for the sol used are given in Table 2.1. Sol **2** has 13.3 wt% Ti compared with 6.0 wt% for sol **1**. Features patterned with sol **2** using a 200 x 200 nm mold exhibited an approximate 30% reduction in volume loss when compared to features patterned with sol **1**. These results are summarized in Table 2.2.

Sol	Ti(OBu) 4	Acetyl-acetone	Acetic Acid	2-Propanol	weight % Ti
1	6.7	15.6	1.0	20.0	6.0
2	20.0	2.0	1.0	2.0	13.3

Table 2.1 Molar equivalents for the formulations of titania sols.

Sol	%x-y shrinkage	%z-axis shrinkage	% Volume Loss
1	57	66	94
2	14	50	63

Table 2.2 Comparison of shrinkage and volume loss for TiO_2 sol formulations. Characterization data obtained from SEM micrographs.

In order to obtain high fidelity patterns over large surface areas, volume loss must be minimized. Significant shrinkage after calcination can lead to loss of pattern details and severe cracking. By altering the sol-gel chemistry, it is possible to control the extent of feature reduction upon calcination.

Due to the nature of the patterning process and the extremely low surface energy of the PFPE elastomer utilized in PRINT, the substrate onto which patterns are created can be varied. Shown in Figure 2.6 are SEM micrographs of titania features embossed onto glass, ITO coated glass, and fluorine tin oxide (FTO) coated glass. Apparently the substrates used have little affect upon the ability of the PFPE mold to form a pattern using the sol-gel route. It can be seen from Figure 2.6 that all of the patterns shown have flash layers with various thicknesses. In photovoltaic applications, a flash layer is needed in order to prevent contact between two electrodes in a layered device configuration. In other applications a flash layer is not desired; however, the PRINT molding process is sufficiently flexible to be used in both situations.^{3,7}



Figure 2.6 SEM micrograph of anatase TiO_2 features replicated on (A) glass, (B) ITO coated glass, and (C) FTO coated glass.

Other important aspects of PRINT are the ability to pattern various shapes, sizes, multiple layers, and a host of different materials. Pattern replication is not limited to structures with low aspect ratios. Silicon masters with cylindrical posts that are 200 nm in diameter and 600 nm in height have been molded and replicated in titania, as shown in Figure 2.7. Due to lateral shrinkage, the anatase TiO_2 posts have an aspect ratio of approximately 2.5.



Figure 2.7. TiO_2 features replicated from a 200 x 600 nm master.

One significant advantage of soft lithography over hard imprint methods is the ability to deposit multiple layers without destroying the pattern of the first layer. An example of the inherent flexibility of the mold in soft lithography is shown in Figure 2.8, where a second generation of titania posts have been patterned on top of a first generation. The intriguing pattern generated by the double PRINT process is a Moire pattern that results from the imperfect orientational alignment of two hexagonally-patterned arrays of features. The double PRINT technique offers the potential to increase both the height and density of features without having to fabricate an expensive new silicon master.



Figure 2.8 SEM micrograph of a double stamped TiO_2 pattern from a 200 x 200 nm mold. Inset taken at a 30° tilt.

Due to the chemical resistivity of the PFPE mold does not limit patterning is not limited to TiO_2 sols. A wide range of metal oxides can be obtained and patterned from sol-gel precursors. Tin oxide (SnO₂), a transparent semiconductor, has recently been investigated for optoelectronics, hybrid microelectronics, and solar energy conversion applications.¹ Many of these applications would benefit from the ability to pattern regular arrays of SnO₂ particles over a large surface area. Using a tin chloride precursor, a SnO_2 sol has been obtained and used for patterning. Arrays of SnO_2 features generated from a 200 x 200 nm mold are shown in Figure 2.9 (A).

Zinc oxide (ZnO) is a stable, wide band gap semiconductor with good electrical conductivity. Various devices employ thin films of ZnO such as piezoelectric transducers, solar cells, and gas sensors.⁵ In particular, improved performance in solar cell and gas sensor applications could be achieved if highly ordered arrays of ZnO features were fabricated. A ZnO sol has been obtained using a zinc acetate precursor, and features have been generated from a 200 x 200 nm mold, shown in Figure 2.9 (B). Unlike the TiO₂ and SnO₂ features, these patterns are not sharply defined. This sol formula uses diethanolamine (DEA), which has a boiling point that is above the drying temperature of the oven used. This may account for the deformed features observed in Figure 2.9 (B).



Figure 2.9 Arrays of metal oxide features on glass made from a 200 x 200 nm mold and (A) SnO₂; (B) ZnO; (C) ITO; (D) BaTiO₃.

Indium tin oxide (ITO) is commonly used as a transparent conductor in electronic, optoelectronic, and mechanical applications such as window heaters, solar cells, and liquid crystal displays.⁴⁰ ITO features have been patterned using a sol derived from indium nitrate and tin chloride precursors and are shown in Figure 2.9 (C).

Barium titanate is a ferroelectric ceramic used largely for its dielectric, piezoelectric, and optical properties. It is used extensively as the filler component in polymer/ceramic composites. The ability to control the shape, orientation and size of dielectric heterostructures is of paramount importance to applications such as sensors, current limiters, acoustic actuators, microwave absorbers,² and the fabrication of photonic band gap structures.⁴¹ The BaTiO₃ features shown in Figure 2.9 (D) were patterned from a sol comprised of barium acetate and titanium isopropoxide based sol using a 200 x 200 nm PFPE mold.

2.3.2 Anodized Alumina Master Template: Fabrication and Replication

Figure 2.10 is a schematic representation of the process used to create the pAAO masters. The first anodization results in only hexagonally close-packed (HCP) ordered pore *bottoms* due to mechanical stresses of the growing oxide layer.⁴² When viewed from the top, there is a disordered array of pores on an uneven alumina surface, as shown in Figure 2.11A. Depending on the analyte used, optimal conditions are needed in order to achieve a high degree of order at the pore bottoms.²¹ It has been demonstrated that for 0.3 M oxalic acid, optimal anodization conditions for a high degree of order are 0 °C and 40 V.²⁰ Although we were unable to hold our samples at a constant 0 °C, it was found that a temperature of 5-7 °C resulted in an acceptable ordered HCP structure with several 'grain-boundary' defects like that of figure 2.11B, while room temperature oxidations

resulted in a disordered structure. After removal of the first anodized layer, the dimpled aluminum substrate was oxidized under the same conditions as the first, while controlling the time to vary pore the depths (Table 2.3).



Figure 2.10 Schematic illustration of two-step anodization process. The first anodization process results in a disordered porous structure on the surface of the Al_2O_3 but produces a hexagonally close-packed array of dimples at the Al/Al_2O_3 interface. After etching away the first oxide layer, the HCP array remaining on the Al is used as a template for ordered growth during the second time controlled anodization.



Figure 2.11 SEM of the pAAO surface (A) after the 1st anodization at 40 V in 0.3 M oxalic acid for 3 hours and (B) and after the second anodization step at 40 V in 0.3 M oxalic acid for 60s. Scale bars are 500 nm.

The ordered pAAO films were analyzed by SEM in order to obtain the cell and pore diameter and depth (see Table 2.3). Anodization at 40 V results in an average cell size of 100 nm and an average pore diameter ranging from 20-50 nm. By controlling the time for the second anodization, the pore depth can be controlled, with longer anodization times resulting in deeper structures. In order to fabricate pores with depths under 100 nm, relatively short anodization times must be employed. As Table 2.3 shows, after 30 seconds of anodization, the pores have already grown to 70 nm deep. From the cross sectional SEM images in Figure 2.12, it is evident that inner pores are not perfectly straight-sidewall cylinders. The pore shape has a 'necking' effect, which has been documented in the literature.⁴³ An etchant solution of 5 wt.% phosphoric acid can be used to remove the pore-necks. However, this also has the effect of enlarging the pore sizes, and causing the 'walls' between the pores to become thinner.



Figure 2.12 AFM image of ordered pAAO template and cross-section SEM of ordered pAAO template (left) whose second step anodization times were 3 min. (top right) and 5 min. (bottom right) in 0.3M oxalic acid. The samples were prepared by simply bending the flexible aluminum substrate, which fractured the thin, brittle, nanostructured pAAO layer.

Time (s)	Pore Depth (nm)
15	55
30	70
45	95
180	131
300	220

Table 2.3. Pore depth vs. anodization time for the second anodization time at 40V. Depths were determined by SEM.

Ordered and non-ordered pAAO masters were produced using either a one or twostep anodization process. These structures were then used in the PRINT process to replicate the structures in TiO_2 . Figure 2.13 shows TiO_2 xerogel patterns replicated from the ordered and non-ordered pAAO templates. From a top-down SEM, the replication appears to be very good in the xerogel state. Pore diameters and order are replicated well for both samples.



Figure 2.13 TiO₂ xerogel patterns replicated from disordered pAAO (left) and ordered pAAO (right). Scale bars are 2 μ m.

As stated previously, TiO_2 nanostructures are more desirable when in either the anatase or rutile crystalline form for use in most applications. Due to the feature reduction that occurs for TiO_2 when going from the xerogel to a crystalline network, there are many defects in the anatase pAAO patterns. From the left image in Figure 2.14 it can be seen that the depth of features for the TiO_2 anatase pattern are not as deep as the original master template. Additionally, due to the non-flat nature of the pAAO templates, it is impossible to get an even flash, or scum, layer on the PFPE molds. This results in a rather thick scum layer for the xerogel, which upon calcination leads to cracking defects throughout the pattern.



Figure 2.14 Anatase TiO_2 patterns replicated from ordered pAAO templates. (left) a high magnification image of the cracking that occurs. The crack allows for the cross-section of the pores to be analyzed, which show extremely shallow pore depths. The SEM image on the right depicts the large area cracking defects that occur throughout the patterned area.

Templates of pAAO provide many advantageous for use as a master template when fabricating sub-100 nm structures. The ordered nature of the pores allows for the fabrication of various sized features with extremely high aspect ratios. Aluminum oxide is a high modulus material that is relatively stable in most contact with most materials used for electronic and photonic applications (when not in the presence of strong acidic or basic conditions). The cost and availability of fabricating pAAO templates is also very reasonable for an academic or small industrial R&D lab; the only equipment required is a controlled temperature bath, leak proof electrochemical cell, stirring apparatus, a power source with controlled voltage, and the aluminum foil starting material. However, there are several drawbacks that limit the use of ordered pAAO as a template for nanofabrication purposes. Aluminum substrates have a large surface roughness, which remains significant even after electropolishing. Related to surface roughness is the issue of obtaining ordered, defect-free patterns over large areas. In order to fabricate ordered arrays over a large area, a constant temperature and acid concentration must be maintained over the entire area of the substrate. There is a company (Synkera technologies inc.) and several groups dedicated to using pAAO as a nanofabrication template, and therefore are putting forth strong efforts to resolve these issues.^{44,45} For our purposes, pAAO proved to be a limited master template for fabricating defect-free nanostructures in TiO₂ over large areas.

2.3.3 Patterning π -Conjugated Polymers

Using the same techniques shown in Figure 2.1, the PRINT process can also be extended to patterning π -conjugated polymers (such as those shown in Figure 2.15) with semiconducting properties. The SEM's shown in Figure 2.16 depict several different polymers, on various substrates, all patterned from low wt.% solutions. These results serve as a proof-of-concept in using PFPE molds to control the nanostructure of polymers that contain drastically different solubilities. All of the patterns were formed using a solvent assisted molding technique, in which a low wt.% solution was simply dropcast onto a substrate. The gas permeable PFPE mold containing recessed cavities was then placed on top of the liquid polymer solution, and the solvent was allowed to evaporate through the mold cavities, effectively filling the nanostructures as the polymer dried. The use of vacuum conditions may be used to increase the rate of evaporation. Though other methods have been used to pattern some of these materials, the PRINT technology is unique in several aspects: (i) it is easily scaled to a roll-to-roll manufacturing process (ii) it is amenable to a wide variety of materials (iii) nanofabrication procedures occur at ambient conditions and (iii) There is no need for the use of expensive, state-the-art facilities required for NIL, SFIL, and traditional photolithography setups (although NIL is expensive and requires cumbersome and highly precise equipment, it is still significantly less cost prohibitive than using a state-of-the-art photolithography facility).

Figure 2.15A shows 150 x 500 nm cylindrical features patterned in poly[2methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) on a poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) coated ITO substrate. It is worth noting the bilayer polymer nanostructure. The ability to solution process multilayered structures is of critical importance for device optimization.³⁸ The features were patterned over a large area (several in.²) by using the solvent-assisted molding technique in which the polymer solution was allowed to dry while in contact with the PFPE mold. MDMO-PPV is a commonly used polymer for photovoltaic devices, where there is a need for controlling the nanoarchitecture of the polymer.⁴⁶⁻⁴⁸

Figure 2.15B shows 150 x 500 nm structures in the water-soluble polythiophene poly[2-(3-thienyl)-ethoxy-4-butylsulfonate] (PTEBS:Na⁺) on an ITO substrate. As a proof of concept, an area that contained a scum-free array is shown. Due to the non-wetting characteristics of water with the PFPE molds, these features were able to be formed in a scum-free array on certain areas of the pattern. Although the pattern encompasses a large area, defects in the flash layer were present across the patterned surface. This engineering issue can certainly be resolved with the use of more precise instrumentation and processing parameters. The application of PTEBS:Na⁺ in photovoltaic devices has been investigated for its application in photovoltaic devices.⁴⁹

Figure 2.15C shows 150 x 500 nm cylinders of the popular semiconducting polymer poly (3-hexylthiophene) (P3HT) on an ITO substrate. The SEM image allows you to see the formation of the crystalline domains in the nanostructures and in the scum layer, which have been shown to form in the literature. The crystalline domains are formed as the system dries and the solvent is evaporates through the mold. The P3HT

polymer has been rigorously investigated for its use in organic photovoltaic (OPV) devices, of which it is the primary component of state-of-the-art OPV devices.⁵⁰⁻⁵³ Only very recently have Yu and coworkers synthesized an alternative polymer that outperformed P3HT based devices.⁵⁴ In addition to OPV applications, P3HT has also been used as the conducting layer for applications in organic thin film transistor (OTFT) devices.⁵⁵



Figure 2.15 Chemical structures of the various polymers patterned in this study. MDMO-PPV, PTEBS:Na⁺, P3HT and the copolymer of a thermally deprotectable polythiophene derivative, TDPTD.

Figure 2.1D shows 150 x 500 nm cylindrical features patterned in a thermally deprotectable polythiophene (TDPTD), of the alternating copolymer poly(3-(2-methyl-2-hexylcarboxylate)thiophene-co-thiophene) on a glass substrate. This polymer was first used by McGehee and co-workers for use in titania-polymer PV devices.⁵⁶ Kim and co-workers at the University of Michigan used NIL to pattern TDPTD as the donor material

in OPV devices. ⁵⁷ Upon patterning in the high temperature NIL process, the ester linkage is cleaved (Figure 2.15) to yield the insoluble carboxylic acid, which is then coated with PCBM via spincasting from chlorobenzene solvent. The ability to tailor the solubility of TDPTD makes it an attractive polymer for many optoelectronic devices in which multilayered structuring is a desire. Using PRINT, we have been able to control the nanostructure of the polymer at uniform temperature and pressures. In addition, the polymer is patterned over large areas, and with a non-existent flash layer.



Figure 2.16 SEM images of 150 x 500 nm cylinders comprised of (A) MDMO-PPV on a PEDOT:PSS coated ITO substrate (B) the water soluble polymer PTEBS:Na⁺ (C) the semi-crystalline polymer P3HT and (D) the thermally deprotectable thiophene alternating copolymer TDPTD.

To prove the ability to form isolated features from the polymers shown in Figure 2.15B and D, microparticles have also been fabricated from these structures. Figure 2.16 shows fluorescence images of TDPTD and PTEBS:Na⁺ microparticles fabricated from a

5 μ m x 10 μ m cubic mold. It should be noted that no dyes were added to the particles, as they naturally fluoresce in the visible due to their conjugation. Both types of particles were formed using the same procedure. A low wt.% solution of polymer in solvent was cast onto the mold, and subsequently laminated with a poly(ethylene) (PE) sheet. The PE sheet was then peeled off the mold to remove the residual scum layer, leaving a the microcavities of the mold filled with a low wt.% polymer solution. The solvent was then removed via vacuum, and the mold was allowed to dry. The filled mold was then laminated to a methylcyanoacrylate layer on a glass slide, and the mold was subsequently removed after the methylcyanoacrylate was allowed to cure. The particles remained adhered to the poly(methylcyanoacrylate) harvesting layer, as the images on the left in Figure 2.16 indicate. The images on the right were obtained by dissolving the adhesive with acetone, and imaging the microparticles while floating through the solution. It can be seen that the height of the PTEBS:Na⁺ particles is much greater than the TDPTD microparticles. The TDPTD particles are shorter because a lower wt.% polymer solution was used to fill the mold and therefore less material remained after removing the solvent. It should be noted that the TDPTD images are of the carboxylic acid version, as these particles were annealed while in the mold to form the insoluble form of the polymer. Isolated micrometer and nanometer particles of polymers are also of interest for the biological community for applications in sensors and drug delivery.⁵⁸

TDPTÐ





Figure 2.17 Fluorescence images of (left) 5 x 10 μ m particles in a poly(methylcyanoacrylate) adhesive used as a harvesting layer and (right) dispersed in an acetone solution.

2.4 Conclusions

In summary, the PRINT technique has been extended to patterning of isolated features as well as embossed films of sub-500 nm features in inorganic oxides including TiO₂, SnO₂, ZnO, ITO, and BaTiO₃. The versatility of this soft lithography method allows patterns to be generated on a variety of substrates including glass and transparent conductive oxides. Volume loss upon calcination has been observed for all sol-gel formulations though the extent of shrinkage can be controlled through tailoring of the sol chemistry. PRINT provides a facile route for patterning features with high aspect ratios as well as layer by layer deposition without destruction of the first layer.

In an effort to extend replication into the sub-50 nm regime, pAAO master templates were fabricated that contained ordered pores in an HCP arrangement over large areas. Using a two-step anodization procedure, 20 nm pores were fabricated. The structures were successfully replicated in a TiO_2 xerogel material. Upon calcinations, the thermal contraction of the xerogel and the thickness of the flash present caused large area defects to occur.

We also were able to construct ordered arrays of 150 nm diameter x 500 nm height cylindrical structures over large areas. Patterns were formed from π -conjugated polymers that show semiconducting properties. Being able to spatially control the deposition and nanoarchitecture of these particles on surfaces is of much importance for organic based optoelectronic devices. We successfully demonstrated that the PRINT process can be used with aqueous-based solutions as well as organic based solutions for nanofabrication of polymers with drastically different solubility parameters. In addition, we are able to extend from fabricating patterned nanostructures on a surface to fabricating isolated particles on the micron length scale.

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Chapter 3

Photovoltaic Applications

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3.1 Organic Photovoltaic Background

Most solar cells that are in use today are normal p-n junctions in a semiconductor across which a photovoltage is developed. Currently, the most successful material for the semiconductor in a photovoltaic (PV) device is crystalline silicon, which comprises 99% of all current solar modules.¹ In fact, ever since the first solar cell was designed at Bell Labs in 1954,² the solar cell industry has been dominated by silicon. The primary reason silicon is used in most PV systems is that it has been highly developed and purified due to advances in the microelectronics industry. Though silicon is the most used material, it is not necessarily the best for a PV device due to an indirect band gap.³ Additional issues associated with silicon include raw material and processing costs.⁴ As material demand for photovoltaics and microelectronics both increase, the price of obtaining and processing silicon is expected to climb.

Considering the cost and problems of the current technology, the thought of thin film plastic solar cells formed by printing and coating techniques (such as reel to reel processing) for large areas is an attractive alternative. Solution processable organic and inorganic semiconductors have the potential to fulfill these requirements. Until recently, there was little interest in organic-based PV devices due to low device efficiencies on the order of 0-1 % and device manufacturing difficulty. With the advent of the dyesensitized solar cell (DSSC) in the early 1990's by Gratzel et al. achieving 10% efficiency, there has been a spur of interest in developing organic based solar cells.⁵

The DSSC operates under a different photoconversion mechanism than traditional inorganic solar cells. Instead of using one material to undergo both light absorption and

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charge carrier transport, the DSSC separates these processes by using several different materials. The electron transport material is usually a mesoporous network of anatase TiO_2 , though other inorganic oxides such as ZnO have been used with less success.⁶ The nanoporous titania is cast in a film with a thickness on the order of 10 μ m. A monolayer of a ruthenium-based dye is then adsorbed onto the surfaces of the nanocrystalline titania to harvest the solar energy. Upon absorption of light, the dye molecule adhered to the titania injects an electron into the TiO₂ conduction band with high efficiency. The electron then migrates through the titania network to the anode, and the dye is regenerated by an electrolyte (also known as hole transport material, HTM) containing a redox couple.

The highest efficiencies have been achieved using a liquid ionic electrolyte as the hole transporting material.⁷ Many problems arise with the liquid electrolyte that may affect device stability such as evaporation, water or oxygen permeation, and sealing issues.^{8,9} Another problem with using a liquid electrolyte is that it makes the processing of multi-cell modules difficult due to the need to separate the cells chemically yet connect them electrically.¹⁰⁻¹² There have been successful attempts recently to replace the liquid electrolyte with elastomeric polymers or gelators filled with an ionic redox couple,^{13,14} and by p-type organic or inorganic semiconductors.^{5,7,13,15} A particularly attractive technique, and the one taken here, is to replace the dye/electrolyte setup with a semiconducting polymer.

Purely organic photovoltaic (OPV) devices which feature two semiconducting polymers as the donor and acceptor materials have also been devised; these originate from the classic p-n junction morphology, or "bilayer" device. Figure 3.1 is an energy

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level diagram of an organic based bilayer device using two different semiconducting polymers. In this type of device, charge generation is initiated by the absorption of light in the donor layer which promotes an electron from the high occupied molecular orbital (HOMO) to the lowest occupied molecular orbital (LUMO) level of a material. The excited electron leaves behind a hole in the HOMO level, creating an electron/hole pair. The electron and hole are coulombically bound to each other and thus are a neutral entity, an exciton, which cannot be affected by an electric field. The exciton must dissociate and the electron must reach one electrode while the hole reaches the other electrode. Exciton dissociation occurs at the donor/acceptor interface and therefore is limited by the surface area of the junction. The diffusion of the exciton to the interface must also occur before the electron relaxes back to its original state (either by phonon resonance or radiative absorption). An important aspect to creating a high efficiency OPV device is to be able to control the device architecture and materials such that both exciton dissociation and light absorption can be maximized.



Figure 3.1 Energy diagram of a bilayer OPV. Exciton dissociation occurs at the donor/acceptor interface and energy levels are aligned such that charge carriers are drawn to their respective electrodes. (Reprinted with permission from reference 16. Copyright © 2004, Elsevier)

Both organic-organic bilayer (Figure 3.2b) and hybrid inorganic-organic solar cells have less than ideal efficiencies due to problems inherent in the device architecture. In the nanocrystalline-titania and conjugated polymer cells, the polymer has a hard time infiltrating the mesoporous nanocrystalline titania network, and therefore does not create a high surface area interface to generate many charge carriers.¹⁷ In organic-organic bilayer devices, the light absorbing layer must be sufficiently thick to absorb as many photons as possible. But a thicker layer also results in excitons being formed further away from the interface where charge separation occurs. These problems in the device architecture of the donor/acceptor interface.



Figure 3.2 Evolution of the organic solar cell. A) a single layer junction in which exciton dissociation occurs at the electrode interfaces B) bilayer device with a donor and acceptor layer C) disordered bulk heterojunction and d) idealized ordered bulk heterojunction with features on the order of 10 nm. (Reprinted with permission from reference 18. Copyright © 2004, American Chemical Society)

It is believed that if the morphology in a bulk heterojunction (BHJ) is such that any point in the network is within an exciton diffusion length of a donor/acceptor interface (Figure 3.2d), then high efficiencies can be achieved.^{16,17,19-21} Most of these BHJs are formed by spin casting solutions made of the two semiconducting materials.²²⁻²⁶ To date, BHJs have had a lack of order and uniform interdigitated morphologies on the nanoscale which have led to low efficiencies. These low efficiencies are caused by problems such as phase separation,²¹ small active areas,¹⁶ and isolated or trapped portions of the network that are not connected to respective electrodes.²⁷ Though optimal device architectures have been attempted as in Figure 3.2d, typically far less ideal structures such as that in Figure 3.3 are obtained.



Figure 3.3 Actually realized controlled bulk heterojunction (BHJ) devices. Sintered TiO_2 nanocrystals that comprise a thin film (left).(Reprinted with permission from reference 18. Copyright © 2004 American Chemical Society). Surface of copper phthalocyanine film with continuous wetting layer plus short needle-like crystals grown on Si. by Yang and Forrest et. al (right). Scale bar represents 500nm. (Reprinted with permission from reference 28. Copyright © 2004, Nature Publishing Group)

3.1.1 Introduction

Conjugated polymers are promising PV materials because they are strong light absorbers, are solution–processable, and can be deposited onto flexible substrates at low cost. To date, the most efficient polymeric solar cells utilize a disordered bulk heterojunction (Figure 3.2C), in which the conjugated polymer is mixed with an electron acceptor.²⁹⁻³¹ During processing, the mixture automatically phase-separates into nanoscale domains with a length scale on the order of the exciton diffusion length (ca. 10 nm), maximizing the exciton collection efficiency. Unfortunately, when different material systems are used, the phase separation distance might change. The morphology of the blend depends critically on numerous processing variables, such as the sidechain length of the polymer, the weight ratio of materials, the choice of solvents, molecular weight, regioregularity, and annealing conditions.^{32,33} Even when we have a phase separation length scale on the order of the exciton diffusion length, each phase in the blend may contain dead-ends, which could hamper the charge collection efficiency.

Ordered BHJs (Figure 3.2B) made by filling inorganic nanostructures with organic semiconductors have distinct advantages over their disordered counterparts because the morphology can be precisely controlled.^{18,19,34-37} Metal oxide (TiO₂, ZnO, etc) templates can be fabricated with continuous pathways or pores on the scale of the exciton diffusion length in the organic semiconductor. Consequently, these devices possess the ideal morphology for maximizing charge collection efficiency, regardless of the polymer used.

Titania is an attractive material for ordered BHJ PV cells for many reasons: it is abundant and non-toxic, it has a low-lying conduction band that can accept electrons from almost all organic semiconductors,³⁸ and its surface can be easily functionalized with organic molecules that facilitate exciton dissociation and charge transfer.³⁹ Also, titania has been well-studied by the dye-sensitized solar cell community.^{5,15}

The ideal titania nanostructure in an ordered heterojunction should be approximately 200-300 nm-thick and consist of an ordered array of titania posts or pores with 10-20 nm spacing (approximately twice the polymer exciton diffusion length⁴⁰).¹⁸ With this geometry, every exciton formed in the donor material is able to reach the interface and be split into two distinct charge carriers. The channels should also be straight and perpendicular to the substrate so that both charge carriers have a direct pathway to their respective electrode. Previously, titania nanostructures have been made using a variety of techniques, including doctor blade spreading of titania paste,²² spray pyrolysis of titanium alkoxides,⁴¹ and evaporation induced self-assembly of titania solution precursors with an amphiphilic block copolymer as a structure-directing agent.⁴²⁻

Instead, the pores are tortuous and the polymer chain packing is disrupted, decreasing hole mobility and thus reducing device performance. Coakley et al. specifically describe how Poly(3-hexylthiophene) (P3HT) mobility is decreased when infiltrated into mesoporous titania films.⁴³ Recently, in an attempt to fabricate straight TiO₂ pathways, anatase phase TiO₂ nanorods were employed in a blend for use in conjuction with P3HT as a polymer-titania device.⁴⁵ One technique for optimizing the nanostructured morphology is nanoimprint lithography,⁴⁶⁻⁴⁸ a promising method due to its high throughput capability to produce nanoscale features over a large area. Whitesides et al. have used polydimethylsiloxane (PDMS) molds to pattern sol-gel derived inorganic oxides into continuous membranes with nanoscale features and into discrete objects at fractions of a millimeter length scale.⁴⁹⁻⁵¹ After gelation of liquid sol-gel precursors, the PDMS molds were removed and the patterned structures were annealed at high temperature. While features as small as 30 nm have been reported, the process is limited by deformations such as feature coalescence, sagging, and swelling of the elastomeric PDMS mold. Another approach towards sub-100 nm pattern replication in titania employs polymethylmethacrylate (PMMA) molds with a PDMS backing layer for added flexibility.²⁰ The high compression modulus of PMMA prevents mold deformation and allows for higher-resolution patterning. However, in this method, mold retrieval requires the wet-etching of the master template followed by dissolving the mold away from the inorganic pattern. The non-reusable nature of the master and the mold make this method unsuitable for large scale manufacturing.

As stated previously, the use of perfluoropolyether (PFPE) elastomers as a reusable molding material for soft lithography has been reported by Rolland et al.⁵²

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PFPE elastomers as molding materials are unique over their silicone-based counterparts in four distinctive ways: (i) the very low surface energy of PFPEs enables the selective filling of nano-scale cavities in the mold with almost any organic liquid; (ii) unlike silicones, fluoropolymers are resistant to swelling in common organic solvents, making them useful for patterning a wide range of organic and inorganic features; (iii) the chemical inertness of the PFPE molds allows the resultant array of features to be easily separated from the mold; and (iv) the modulus of the elastomer can be tuned by precursor molecular weight, allowing for patterning of a wide variety of sol-gels into sub-100 nm features. Pattern Replication in Non-wetting Templates (PRINT) shows great potential for controlling device architecture in ordered BHJ solar cells.

In this chapter, we present the use of PRINT for patterning anatase TiO_2 on a sub-100 nm length scale (see Figure 3.6). The ordered BHJ devices, made by infiltrating titania nanostructures with P3HT, show a two-fold improvement in short-circuit current relative to flat bilayer devices. In addition, we use PFPE molds to fabricate nanostructures from a polythiophene derivative for use in all-organic OPV devices. The nanopatterned all-organic devices show a 33% improvement over the flat bilayer devices.

3.2 Experimental

3.2.1 Materials and Characterization Techniques

All chemicals were purchased from Sigma-Aldrich except the Z907 dye (Solaronix SA), poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) (Baytron PH 500) and the poly(3-(2-methyl-2-hexylcarboxylate)thiophene-co-thiophene) which was obtained from Lei Zhang. All chemicals were used as received except P3HT, which was purified by Soxhlet extraction using hexane and then chloroform. The

synthesis of perfluoropolyether dimethacrylate (PFPE DMA) has been reported previously.⁵² The photoinitiator used to cure the PFPE DMA was 2,2diethoxyacetophenone (DEAP). Metal oxides were characterized with an X-ray diffractometer (XRD, Rigaku) using Cu K α radiation. Scanning electron microscope (SEM) images were obtained with either a Hitachi S-4700 instrument or a FEI Helios 600 NanoLab Dual Beam System. 200 nm x 600 nm cylindrical and 80 nm x 90 nm grating style master templates were obtained from Liquidia Technologies.

3.2.2 Master Template Fabrication

Nanosphere Lithography (NSL) Master: A monolayer of polystyrene nanospheres (diameter 26 ± 5.5 nm, concentration 4.1 g/100 mL, purchased from Interfacial Dynamics Corp.) was deposited on a silicon wafer by first diluting the original solution of nanospheres two-fold and then spin-casting at 5000 rpm. A 5 nm layer of chromium was evaporated on the nanosphere monolayer using electron-beam evaporation. The spheres were then dissolved by sonication in heated toluene for 1 - 2 hr. The exposed silicon surface was etched using NF₃ reactive ion etching (RIE) (20 sccm NF₃, 20 mTorr chamber pressure, 430 V bias voltage) in an AMT 8100 Plasma Etcher. RIE times of 3 and 4 min were used. The nanopillar surface was cleaned using a UV-ozone treatment. Any remaining chromium was removed using a standard piranha etch (80% conc. sulfuric acid and 20% hydrogen peroxide, by volume). A similar process using a block-copolymer as the etching mask was reported elsewhere.⁵³

3.2.3 PFPE Mold and Membrane Fabrication

For the TiO₂ devices and replication, a liquid 1kDa PFPE DMA (α , Ω -functionalized dimethacrylate) precursor solution containing 1 wt% DEAP was poured

over a NSL patterned master template or a piranha cleaned silicon wafer. For the polymer nanostructures and devices, a 4kDa PFPE DMA $\Omega(\alpha, -$ functionalized dimethacrylate) precursor solution containing 1 wt.% DEAP was poured over a patterned silicon master. The liquid precursors were then crosslinked using UV photoirradiation ($\lambda = 365$ nm) for 3 min under a constant nitrogen purge to provide an elastomeric mold of the master template. The fully cured PFPE DMA elastomeric mold or flat membrane was then released from the respective silicon master.

3.2.4 Sol-gel synthesis

To make titania sol **1**, a 0.46 mL portion of titanium ethoxide was combined with 5.1 mL of 2-propanol. After several minutes of stirring, 0.18 mL of concentrated hydrochloric acid was added dropwise to the solution. The sol was stirred for 1 h and filtered through a 0.45µm filter before use. To make titania sol **2**, 9.0 mL titanium butoxide was combined with 0.27 mL acetylacetone. After stirring for 15 minutes, 0.20 mL of 2-propanol was added to the solution. A 0.075 mL portion of glacial acetic acid was added dropwise to the stirring solution. The sol was stirred for 1 h and filtered through a 0.45µm filter before use.

3.2.5 Titania Nanostructure Fabrication

The glass / fluorine doped tin oxide (FTO) substrates (AFG Industries Inc., 100 Ω/\Box) were cleaned by first scrubbing with a dilute solution of Contrex AP detergent, rinsed with deionized water, followed by sequential sonication in acetone and isopropanol. After drying the substrates at 110°C in air and UV-ozone cleaning them for 15 min, a thin film of sol **1** was deposited by spin casting the sol at 2000 rpm. These samples were then oven-dried at 110°C for 12 h prior to being calcined at 450°C for 30

min using a ramp-rate of 5 °C/min. Sol **2** was then drop-cast onto the substrate and either a flat PFPE membrane or a patterned PFPE mold was pressed into the liquid sol. The sample was held at constant pressure at 110° C for several hours. The mold was then removed, and the samples were heated to 450°C at a rate of 10°C/min and held at 450°C for 30 min to crystallize the titania.

3.2.6 Photovoltaic Device Fabrication

 TiO_2 devices: The freshly-calcined titania was treated with a UV-ozone clean for 10 min. Subsequently, a layer of heat-curable polyimide was applied to one edge of the titania film. The polyimide was heated for 10 min each at 60 °C, 90 °C and 140 °C, after which it was cured. The non-dye coated samples were promptly transferred into a glove-box filled with nitrogen. Some samples were first treated with the interfacial modifier (Z907), as reported previously, before being transferred into the glovebox.⁵⁰ For both the nanostructured and reference devices, a 100-nm-thick P3HT film was spun-cast from tetrahydrofuran (THF) on top of the titania structures and melt-infiltrated by heating at 185 °C in glovebox for 8 min followed by slow cooling.⁴³ Reflective top electrodes consisting of a 70 nm layer of silver were then thermally evaporated under vacuum (at greater than 10⁻⁶ torr) on top of the polymer film. The use of shadow masks allowed the fabrication of six 3-mm² finger-like devices per substrate. All subsequent device testing experiments were done in nitrogen environment.

Polymer devices: Glass/ITO substrates were cleaned in by sonicating in deionizedwater, acetone, and isopropyl alcohol for 10 min. each. The air-dried substrates were UV-ozone (UVO Cleaner 42, Jelight Company Inc.) cleaned for 10 min. prior to spincasting a layer of previously filtered PEDOT:PSS (0.45µm PVDF filter) at 3,000 rpm. The devices were then annealed at 115°C for 15 min. and transferred to a nitrogen glovebox for the remainder of the device fabrication and testing process. A layer of a thermally deprotectable polythiophene derivative alternating poly(3-(2-methyl-2hexylcarboxylate)thiophene-co-thiophene) (TDPTD) was formed on the PEDOT:PSS coated ITO substrate by spin casting from a 1 wt.% chlorobenzene solution. A PFPEmold was then put into contact with the TDPTD layer, and pressure and heat ($\sim 200^{\circ}$ C) were applied using a jack and a hot plate. After two minutes of annealing under pressure, the assembly was allowed to cool and the mold removed. A 1 wt.% PCBM in chlorobenzene solution was then spun-cast onto the TDPTD nanostructures at 1,000 rpm for 60 seconds. Aluminum electrodes were thermally evaporated (at greater than 10^{-6} torr) onto the PCBM layer. The use of shadow masks allowed the fabrication of eight ~5-mm² finger-like devices per substrate (areas of the devices were calculated using an optical microscope). All subsequent device testing experiments were carried out in a nitrogen environment. All efficiency measurements were performed in inert gas (purified nitrogen) filled glove box at room temperature. Current-Voltage performance was achieved by Keithley 2400 source meter with exposure to a controlled power density of light, made from Oriel-Newport 300 W solar simulator. The solar spectrum was modulated by an AM 1.5G filter without an additional filter. The intensity of the solar simulator was measured by a standard silicon solar cell calibrated by the National Renewable Energy Laboratory.

3.3 Results and Discussion

3.3.1 TiO₂ Devices
3.3.1.1 Fabrication of Master Template by Nanosphere Lithography and Production of PFPE Molds

Nanosphere lithography (NSL) has proven to be a simple yet effective technique to obtain periodic arrays of nanopillars across a large surface area.⁵⁴ By first spin-casting a dilute solution of polystyrene nanospheres on a silicon wafer, a monolayer of nanospheres was readily deposited over the entire surface. These nanospheres are not robust enough to be used directly as an etch-mask for RIE; therefore, a 5 nm Cr layer was deposited on top of the nanosphere monolayer using electron-beam evaporation. The nanospheres were then dissolved by sonication in toluene at 60° C. This process left behind islands of Cr that were used as an etch-mask for nanopillars. The height of the final features in silicon is directly proportional to the time of the RIE (all other conditions remaining constant). The features we obtained were randomly oriented post-like structures with the highest aspect ratio structures having a maximum height of 140 nm and a diameter of 20 nm. The random orientation was due to the large variance in nanosphere diameters (average of 20 nm) which resulted in various sized interstitial holes between nanospheres where the Cr mask was deposited. Any Cr remaining on top of the nanopillars was removed using a standard piranha etch. While the feature shape and distribution across the wafer varied for each sample, this method was effective in generating nanoscale patterns across large areas.



Figure 3.4 Illustration of the PRINT process: (a) Si master template; (b) mold release from master template; (c) molding a liquid precursor; (d) pattern transfer to substrate at elevated temperature and pressure; (e) mold release from replica film.

In order to obtain an elastomer mold of the NSL master template, a liquid PFPE precursor comprised of 1 kDa PFPE ($\alpha \Omega$ -functionalized dimethacrylate) and 2,2-diethoxyacetophenone was poured over the nano-patterned master template. Due to its very low surface energy, the liquid PFPE was capable of selectively filling the nano-scale cavities in the master. Subsequent photochemical crosslinking resulted in a high fidelity mold of the nanoscale features of the NSL master template, as shown in Figure 3.5.



Figure 3.5 3 x 3 μ m atomic force microscope images of the (a) silicon master fabricated via nanosphere lithography and the (b) 1 kDa PFPE elastomer mold of the master template. z-height = 150 nm for both images.

3.3.1.2 Feature Replication in Anatase Titania

When fabricating titania nanostructures for photovoltaic applications, it was necessary to employ two layers of titania on top of the FTO electrode. The first layer was a flat, thin film foundation of anatase titania upon which the nanostructured layer was fabricated. The first thin film of titania provided a pinhole-free layer that prevents device shorting as a result of direct pathways between the top and bottom electrodes. This was especially important if the second (patterned) titania layer had any small cracks or pinholes. Different sol formulations were utilized for the two layers in order to obtain a crack-free thin film in the first layer and to prevent volume reduction and feature degradation in the second layer.

In this process, a thin film of sol **1** as the compact underlayer was deposited onto FTO electrode by spin casting. The samples were then oven-dried and calcined at 450°C. Subsequently, liquid sol **2** was drop-cast onto the sample and a PFPE mold was pressed

down onto the substrate and held at constant pressure. The sample was heated to 110°C to facilitate the sol-gel transition via solvent removal, a process that was aided by the high permeability of the mold. The low-surface energy PFPE mold was then peeled off the FTO substrate, leaving an embossed xerogel film. Calcination of the xerogel phase at 450°C led to the formation of anatase titania features (see Supporting Information). Scanning electron microscopy images of the silicon master template from NSL and resultant titania nanostructure are shown in Figure 3.6.



Figure 3.6 SEM image of (a) NSL silicon master template with 3-min RIE and (b) anatase titania nanostructure replicated using PRINT from the silicon master. Scale bars are 100 nm.

3.3.1.3 Device Fabrication and Solar Cell Performance

As previously described, we employed two layers of titania on top of the FTO electrode to fabricate the nanostructure. Reference cells were also fabricated with two layers of titania to ensure a comparable reference cell for the nanostructure devices. In this case, a thin film of titania was spun-cast from sol **1** and calcined at 450°C. A second film of titania was deposited by first drop casting sol **2** on the substrate and then placing a flat PFPE membrane on top of the sol. The substrate was held at elevated pressure and temperature for several hours, followed by PFPE membrane removal and 450°C calcination of the sample.

After making nanostructured titania samples, a 100-nm-thick P3HT layer was spun-cast on top of the film and infiltrated around the features by heating the sample to 185°C for 8 min in a nitrogen environment. According to previous studies by Coakley et al. the annealing procedure should be sufficient to infiltrate P3HT to the bottom of the pores. Figure 3.7 is a schematic representation of the device stack for a nanostructure device.



Figure 3.7 Schematic diagram showing the cross section of a photovoltaic device where the titania-polymer interface has been patterned using the PRINT technique.

Figure 3.8 shows the I-V curves of the nanostructured titania devices along with the flat reference devices. We observed that the incorporation of the interface modifier, Z907, helped improve the J_{SC} and V_{OC} for both reference and nanostructured devices. We attributed this enhancement to an improvement in exciton splitting at the interface. The carboxylic acid groups covalently bound to the titania surface promoted rapid forward electron transfer, while the long insulating alkyl side chains suppressed charge recombination and promoted wetting of the titania surface by the P3HT.^{37,39,55-57}



Figure 3.8 Current-voltage (I-V) curves of four titania/P3HT systems: flat titania/100-nm P3HT (reference device), flat titania with surface modified with Z907/100-nm P3HT (reference device), nanostructured titania/100-nm P3HT, nanostructured titania with surface modified with Z907/100-nm P3HT.

When comparing devices that received the same interfacial treatments, nanostructuring of the titania increased the short circuit current (J_{SC}) by two fold, while maintaining the open circuit voltage (V_{OC}) relative to the flat film reference devices. Upon nanostructuring, the J_{SC} of the unmodified devices increased from 0.55 mA/cm² to 1.12 mA/cm², while for interface-modified devices, the J_{SC} increased from 0.80 mA/cm² to 1.62 mA/cm². This doubling of J_{SC} agreed well with simple calculations based on increasing the titania/P3HT interfacial area for a hexagonal array of titania posts with dimensions of radius 10 nm, height 100 nm, and periodicity of 60 nm. In addition to increased exciton splitting resulting from the larger interfacial area, other factors could be influencing the photocurrent as well. Charge mobility in the polymer phase may be enhanced due to chain alignment in the nanoscale channels of the nanostructure titania, which would result in an increased J_{sc} .⁵⁸ The nanostructure device with interface

modifier showed $J_{sc} = 1.62 \text{ mA/cm}^2$, $V_{oc} = 0.65 \text{ V}$, fill factor (FF) = 0.55, and overall efficiency of 0.6%, one of the highest efficiencies reported for nanoimprinted titania-P3HT solar cells.

3.3.2 Polymer based devices

Polythiophene-methanofullerene bulk heterojunction cells have shown some of the highest recorded efficiencies to date in solid state organic solar cells.⁵⁹ These disorded networks have much room for improvement if the morphology of the donoracceptor network can be controlled such that exciton splitting and charge carrier collection efficiencies are maximized by forming the ideal device architecture. There have been several attempts to fabricate ordered BHJ's in organic PV systems, in particular a promising technique is to use vapor phase deposition to control the crystal growth of a small molecule 'donor' used in OPV systems.²⁸ Kim et al. have used NIL to pattern TDPTD (Figure 2.15) and were able to fabricate PV devices that had increased efficiencies due to the nanopatterned donor-acceptor interface.⁴⁷ Hu and co-workers at the University of Texas at Dallas have also used NIL to pattern 80 x 200-250 nm posts in P3HT for use in PV devices.^{60,61}

As discussed in chapter 2, the PRINT process is amenable to large area fabrication of ordered arrays of nanostructures in polymeric 'donor' materials. There have been several reports of all organic bilayer photovoltaic devices fabricated using lamination techniques or solution processing. Lamination is a promising method, and has been used by Friend^{62,63} and Whitesides⁶⁴ to fabricate efficient bilayer OPV devices. There have also been several reports of creating bilayer type devices using orthogonal solvents. This allows for solution deposition of the second layer without

destruction of the first layer. These reports include the use of PCBM dissolved in xylenes to coat MDMO-PPV,⁶⁵ PCBM dissolved in dichloromethane to coat P3HT,⁶⁰ and multilayers of PSS/PPV/C₆₀ fabricated using charged substrates and polyelectrolytes to obtain a multilayer structure.⁶⁶

3.3.2.1 Solution Processed Multilayer Donor/Acceptor Interfaces

We have sought to create a multilayer polymer structure to fabricate OPV devices. Following reports in the literature, we first attempted to fabricate multilayered structures of MDMO-PPV/PCBM using a spin casting process to coat the MDMO-PPV nanostructures. Decahydronaphthalene was shown to be a true orthoganol solvent in which the PCBM has a high solubility and the MDMO-PPV essentially had no solubility. Figure 3.9A shows the results when a 1.5 wt.% solution of PCBM in decahydronapthalene was spin cast onto PPV nanostructures. According to SEM and UV-vis, there is no deposition of the PCBM onto the MDMO-PPV nanostructured layer. The non-wetting nature of the decahydronapthalene solvent on MDMO-PPV resulted in complete dewetting, and therefore no PCBM coating. Furthermore, surface tension forces during evaporation of the solvent caused the MDMO-PPV nanostructures to collapse into each other (this effect is often referred to as feature collapse in the semiconductor industry when developing photoresist patterns). Xylenes have also been reported to be an orthogonal solvent for the deposition of PCBM onto MDMO-PPV layers.⁶⁵ Figure 3.9B shows the results of spin casting a 1.5 wt.% PCBM solution in xylenes onto 150 x 500 nm MDMO-PPV cylindrical structures. From the top-down image in Figure 3.9B it appears that the features have been coated successfully. However, the cross-section image in the

upper right shows that the thickness of the layer is ~300 nm. Clearly there is significant destruction of the PPV nanostructures when coating with the xylene solution.



Figure 3.9 150 x 500 nm cylindrical MDMO-PPV nanostructures were spin cast with a low wt.% solution of PCBM in decahydronapthalene (left) and xylenes solvent (right). Scale bars are 500 nm.

Figure 3.10 shows 150 x 500 nm structures in the water soluble polymer poly[2-(3-thienyl)-ethoxy-4-butylsulfonate] (PTEBS:Na⁺). The water soluble polythiophene has been used previously in bilayer solar cell devices in which a C_{60} layer was evaporated onto the donor material under high vacuum conditions.⁶⁷ Figure 3.10 displays the results of attempting to coat the nanostructures coated with a 1.5 wt.% PCBM in chlorobenzene. It is possible to solution deposit the PCBM without destruction of the polymeric nanostructures, however, the chlorobenzene solvent was slightly non-wetting on the Na⁺PT. The non-wetting coating resulted in an uneven deposition and ultimately does not allow for large area fabrication of devices.



Figure 3.10 Attempts to solution deposit PCBM from a chlorobenzene solvent onto 150 x 500 nm cylindrical PTEBS:Na⁺ features. Scale bars are 1 μ m.

In an attempt to find a successful material system for an all-solution processed nanostructured device, we turned to the thermally deprotectable polythiophene copolymer derivative (TDPTD) was investigated. The copolymer has a thermally cleavable ester linkage that forms an insoluble carboxylic acid derivative. As shown in chapter 2, it is possible to fabricate both nanopatterns and microparticles from this polymer. Ko et al. have previously patterned a blend of this polymer with PCBM to form a photonic crystal (PC) enhanced OPV device.⁶⁸

3.3.2.1 Device Fabrication and Solar Cell Performance

To make the nanopatterned TDPTD structure, a PFPE mold was formed from a silicon master containing 90 nm lines, spaced by 90 nm, with 80 nm heights. The mold was used to imprint the ester form of the TDPTD at elevated temperatures of ~200°C, which allowed for cleavage of the ester bond and formation of a grating pattern in the insoluble carboxylic acid form. The nanostructures were coated with the PCBM 'acceptor' material by spin casting from a chlorobenzene solution. 12 mm² aluminum electrodes were then evaporated onto the samples to complete the device.

Preliminary results (Figure 3.11) indicate that the PRINT technology is sufficient in fabricating working solar cells from the TDPTD polymer. The patterned devices show a 33% improvement over the flat, bilayer devices. The PRINT fabricated devices had similar performance to the previously reported nanopatterned TDPTD-PCBM devices, which showed a maximum efficiency of 0.80 % for grating style structures with a 510 nm periodicity and 200 nm depth.⁴⁷ It should be noted that the control devices here outperformed the NIL fabricated control devices significantly, 0.25% vs. 0.70%. Table 3.1 shows that the fill factor is less for the nanopatterned devices. The S-shape of the curve is indicative of significant charge trapping occurring.^{69,70} This is most likely due to the interface between the patterned TDPTD layer and the PCBM. In addition, the V_{oc} is slightly lower for the nanopatterned devices, which also indicates the presence of charge traps in the device structure.







Figure 3.11 Schematic representation of a flat and patterned device and the I-V curves associated with each.

			% change
	Flat	Pattern	(flat → pattern)
J _{sc} (mA/cm ²)	0.89	1.19	33.4
V _{oc} (V)	0.74	0.69	-5.6
F.F. (%)	53.5	51.3	-4.2
η _{eff} (%)	0.70	0.83	19.4

Table 3.1Comparison of photovoltaic properties for the flat and patterned devicesshown in Figure 3.11.

3.4 Conclusions

We reported on the use of nanosphere lithography to make silicon master templates and the PRINT process to replicate the master template structures into anatase titania. We fabricated ordered bulk heterojunction solar cells with nanostructured titania and P3HT. Compared to a flat reference bilayer device, the short-circuit current was doubled upon nanostructuring, while the open-circuit voltage remained the same. The nanostructured device with the Z907 interfacial modification led to a power conversion efficiency of 0.6%. This demonstrates the feasibility of fabricating nanostructured titania solar cells via PRINT, a potentially high-throughput soft lithography route that is amenable to a wide variety of materials and processing conditions. Additionally, further improvement in PV device efficiency could result from using a master template with higher aspect ratios and closer feature spacing, and from infiltrating nanostructures with different materials such as low bandgap polymers.

Bilayer device fabrication consisting of PCBM/nanostructured polymer were attempted using an orthogonal solvents approach. A uniform coating without nanostructure destruction of MDMO-PPV or PTEBS:Na⁺ could not be achieved as opposed to literature reports. A thermally deprotectable polythiophene derivate was able to be used as the nanostructured polymer that allowed for solution deposition of PCBM. PRINT was also used to fabricate grating style structures in TDPTD. Nanostructured devices showed an increase in device efficiency compared to flat bilayer devices.

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Chapter 4

High-resolution PFPE-based Molding Techniques for Nanofabrication

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4.1 Introduction to High Resolution Nanofabrication Techniques

Replica molding that utilizes soft molds has garnered much interest over the past decade as a ubiquitous and versatile nanofabrication technique. A wide variety of polymeric materials such as polyurethanes¹, novolac resins², polyolefins³, UV-curable polyacrylates⁴, and amorphous fluoropolymers⁵ have been employed as mold materials. The primary and most investigated elastomer for nanofabrication is polydimethylsiloxane (PDMS).⁶ There are several reasons that PDMS emerged as the material of choice for soft lithography: (1) A low modulus and surface energy allows for conformal contact and easy release from both masters and patterned materials (2) PDMS is a durable material with fair chemical resistance and is transparent above 280 nm and (3) The most popular form of PDMS, Sylgard 184[®] Dow Corning, is commercially available in inexpensive kits.

Generally, PDMS is a sufficient mold material for most nanofabrication processes involving features on the order of 500 nm. However, there are some inherent disadvantages with Sylgard 184 as a sub-100 nm resolution, high fidelity, mold material. The low modulus of ca. 2 MPa limits the feature size and aspect ratio that can be replicated.⁷ PDMS swells when exposed to some common organic solvents⁸ and many of the organic liquids desirable for molding.⁹ In addition, the high thermal expansion coefficient of PDMS and the fact that Sylgard 184 needs to be thermally cured can result in damage or deformation of features during the pattern fabrication process.

Several types of PDMS materials have been developed to improve mold performance and overcome the disadvantages associated with Sylgard 184. Schmid et al. first developed a higher modulus h-PDMS (E ~ 9 MPa) using short crosslinkers to replicate square posts down to 80 x 80 nm with 100 nm heights and spacings of sub-80 nm.⁷ Though the h-PDMS showed better resolution than the traditional Sylgard 184 for microcontact printing (μ CP), the molds were brittle and susceptible to cracking, delamination, and debris. To overcome problems associated with the h-PDMS molds, Odom et al. formed composite stamps which were composed of two layers – a thin stiff layer supported by a thick flexible layer – that consisted of h-PDMS and Sylgard 184, respectively.^{10,11} Using phase shift lithography, they were able to pattern 50 nm lines, though they were largely spaced at a distance of 2 mm. Rogers et al. developed a photocurable version of PDMS ($h\nu$ -PDMS) to overcome deformations associated with thermal curing of stamps.¹² $h\nu$ -PDMS was used as a mold material to successfully replicate 300 nm width by 300 nm spacing by 600 nm height lines which could not be replicated in either Sylgard 184 (feature collapse failure) or h-PDMS (fracture failure).

In addition to siloxane-based polymers, a wide variety of polymeric stamp materials have emerged that show increased resolution and material compatibility. Campos et. al. recently reported the use of a photocurable poly[(3-mercaptopropyl)-methylsiloxane] (PMMS) thiol-ene-based mold to pattern sub-100 nm structures using a nanoimprint technique.^{13,14} Williams et al. report the use of a nanoimprint composite molding technique that features a high modulus acrylate based molding material used to pattern 15 nm features separated by ~90 nm.^{15,16} The flexible composite molds were also used to pattern 100 nm lines onto curved surfaces. These newly developed mold materials represent exciting alternatives to traditional siloxane-based elastomers. However, the acrylate and PMMS based molds still require fluorine functionalization for

non-destructive release. The acrylate based molds cannot be used to pattern acrylate based photoresists, and require a cumbersome mold fabrication procedure.

One attractive route for imprint lithography and replica molding is the use of fluorinated elastomers. In replica molding, it is quite common to functionalize the surface of the master or mold to lower the surface energy and allow for release of the mold without destruction of features. The DeSimone laboratory pioneered the use of photocurable perfluoropolyether-based (PFPE) materials as an alternative to PDMS for microfluidic and soft lithography applications.^{9,17} Rogers et al. added to this work using similar acryloxy PFPE (a-PFPE) based elastomers in a wide variety of soft lithography methods wherein the a-PFPE outperformed h-PDMS.¹⁸ Fluorinated elastomers are attractive as a mold material due to their low surface energy, solvent resistance, chemical stability, visible transparency and tunable modulus. These characteristics open up the possibility of patterning a wide variety of nanostructures and materials. PFPE molds have been used to replicate nanostructures in materials ranging from inorganic oxides to proteins.^{19,20} Maynor et al. have shown that by changing the crosslink density of the elastomer, the resolution of the molds can be enhanced to replicate objects as small as carbon nanotubes on a surface.²¹ The fluorinated molds have been used in a scalable process called Pattern Replication In Non-wetting Templates (PRINT) to fabricate isolated micro- and nano-particles of controlled shape, size, and chemistry for a variety of life science applications.²²⁻²⁵

For all soft lithography applications, large area masters and pattern fidelity are usually the limiting and most important aspects. There are multiple factors that dictate the fidelity of an elastomeric mold when used in replica molding processes. Various elastic deformations such as roof collapse, buckling, lateral collapse, smoothing, delamination, and edge roughness can constrain the design of molds used for soft lithography.¹⁰ With the goal of increasing the resolution, fundamental limits of patterning have been determined both theoretically and experimentally for PDMS based materials.²⁶⁻³⁰ It should be noted that as features approach the nanoscale, pattern density (and therefore feature spacing) has been shown to play an important role in fidelity.³⁰

This chapter reports the development of various PFPE-based mold materials for high resolution replica molding. Previous studies on PFPE mold fidelity have tested the fundamental size limit of replication, which is determined by the molecular precursors of the polymer. This work investigates the resolution molding materials as determined by the practicality of fabricating ordered, closely spaced structures from master templates whose feature sizes and densities have not been previously realized over large areas due to past limitations in lithography for master fabrication. We have developed novel molding materials that have low surface tension values and relatively high Young's moduli for high-resolution nanopatterning. Composite molds with the active mold material consisting of a high modulus PFPE-TMA were fabricated and used to replicate closely spaced 20 nm structures without the use of heat or pressure. Composite molds have the concomitant effect of increasing performance while reducing the volume of the expensive PFPE-precursor used in each mold. Resolution limits were determined experimentally for high density, closely spaced grating style nanostructures. We also investigate the effect of mold and surface properties on the amount of fluorinated residuals left on a surface by PFPE-based elastomers.

4.2 Experimental

4.2.1 Materials and Characterization Techniques

All chemicals were purchased from Aldrich unless otherwise stated. The synthesis of PFPE-DMA⁹ and PFPE-TMA³¹ has been previously reported. The photoinitiator used to cure liquid PFPE was 2,2-diethoxyacetophenone (DEAP). SEM micrographs were obtained with either a Hitachi S-4700 instrument or a FEI Helios 600 NanoLab Dual Beam System. Moduli were determined from the stress-strain curve with a linear fit from 0 to 2% strain. Stress-strain measurements were performed for rectangular samples at room temperature (ca. 23 °C) on an Instron model 5566 system using a 10 kN load cell at a crosshead speed of 5mm/minute. Static contact angles were measured using a KSV Instruments LCD CAM 200 optical contact angle meter at room temperature (ca. 23 °C). All measurements were carried out with drops that had a total volume of 10 µL on the surface of each fully cured film using a 1000-µL screw top Surface tension values were determined using the Owens-Wendt-Kaelbe syringe. (OWK) method on the side of the elastomer cured to a SiO₂ surface. In the OWK method, water and n-hexadecane were used as the polar and non-polar probes, respectively. Samples were prepared by pooling the PFPE liquid onto a clean, flat, Si wafer and curing in a N₂ environment. The resulting solid elastomeric films were then peeled off of the wafer, and the side of the film that was in contact with the Si substrate was used for contact angle measurement.

4.2.2 Master Fabrication

Master templates comprising hexagonal arrays of Si pillars were fabricated at Hitachi GST, San Jose Research Center using block copolymer lithography. Selfassembled block copolymer thin films were made from poly(styrene-block-methyl methacrylate) (PS-b-PMMA) diblock copolymers (65 kg/mol with ~70% PS content). Upon microphase separation, this polymer self-assembles into PMMA cylindrical domains in a PS matrix. The cylindrical cores have a 38 nm center-to-center separation and a 20 nm diameter. Block copolymer films were applied onto Si substrates previously treated with a hydroxyl-terminated random PS-r-PMMA random brush³² which induces perpendicular alignment of the PMMA cylinders but does not otherwise dictate the orientation of the hexagonally packed polymer lattice within the film. After selectively removing the PMMA cylindrical cores, a ca. 7 nm thick Cr film is deposited on top of the porous PS matrix followed by a lift-off process to remove the PS mask leaving an array of hexagonally-packed Cr dots. A subsequent CF₄ reactive ion etching is used to render ca. 40 nm tall Si pillars.³³

Grating master templates were fabricated at the Center for Nanophase Materials Science at Oak Ridge National Laboratory using e-beam lithography and anisotropic silicon etching techniques. Templates having appoximate 1:1 line width:spacing were prepared by patterning Cr lines on a silicon substrate using conventional lift-off techniques. Briefly, ZEP520A (Zeon Corporation, Tokyo) diluted 1:1 in anisole was spin-coated at 6000 RPM on the silicon substrates and baked at 180°C for 2 minutes. Samples were exposed at varying doses in a JEOL 9300FS electron beam lithography system and developed in xylenes for 30 seconds. Following a brief "descum" in an oxygen plasma, 10nm of Cr was evaporated onto the samples. Lift-off performed via sonication in acetone was used to remove Cr in unpatterned areas, leaving behind Cr gratings of the desired line width and spacing. Etching was performed in an Oxford Plasmalab 100 inductively coupled plasma, reactive ion etcher using a combination of and SF6/C4F8 gases. Etch rates were approximately 100nm/min.

4.2.3 PFPE Mold Fabrication

Composite molds comprised of a patterned, high modulus material with a thick, 4K PFPE-DMA backing were formed by first casting a thin film of the liquid PFPE onto the patterned master templates. The material was then exposed to UV-radiation (λ =365 nm) for 3 min. in an ambient environment. 4K-PFPE-DMA was then pooled onto the partially cured thin film and the sample was again exposed to UV-radiation (λ =365 nm) for 3 min. under a constant nitrogen purge. The resulting composite mold was then peeled off of the master template by hand. Composite molds comprised of a patterned, high modulus material with a PET backing were formed by first pooling a small amount (< 1 mL) the liquid PFPE onto the patterned master template. A flexible PET sheet was placed on top of the PFPE liquid, and the sheet was guided to allow for the liquid to wet the entire area of the patterned master template. The sample was exposed to UVradiation (λ =365 nm) for 3 min. in ambient conditions. The resulting composite mold was then peeled off of the master template by hand.

4.2.4 Preparation of XPS and Contact Angle Samples

SiO₂ wafers were first cleaved into ~1" x 1" square sample sizes and cleaned in a pirhana solution at 80° C for at least 30 min. prior to use. The substrates were rinsed with acetone, distilled water, and methanol before being air dried with a N₂ stream. A PFPE mold was then placed onto the Si-wafer using controlled pressure with a rubber roller. The mold was allowed to sit on the substrate before being removed.

Mold fabrication for XPS and Contact Angle Studies: The liquid PFPE precursor containing 0.1 wt.% diethoxyacetaphenone as a photoinitiator was pooled onto a 3" x 1" pirhana cleaned glass microscope slide. The sample was exposed to UV-radiation ($\lambda_{max} = 365 \text{ nm}$) in a purged N₂ environment.

PEG functionlization: Plasma cleaned silicon wafers were immersed in a 4-5 mmol solution of methoxy(polyethyleneoxy)propyltrimethoxysilane (Gelest) in toluene with 0.8 mL/L HCl (conc.). The samples remained in the solution for 18 h at room temperature to allow for complete fictionalization. Upon removal, the samples were washed in toluene, ethanol, and distilled water prior to being air dried with a N_2 stream.

4.3 Results and Discussion

4.3.1 PFPE Material Properties

It is well known that the modulus and surface tension of a molding material will affect resolution. The modulus of a rubber-like elastomer is inversely proportional to the molecular mass between crosslinks (M_c) for a given polymer. There are essentially three methods that can be used to decrease M_c for a polymeric elastomer; (1) blending the prepolymer with a lower M_w prepolymer or small molecule crosslinker, (2) synthetically lower the molecular weight of the pre-polymer and (3) synthetically increase the functionality of the prepolymer by adding reactive endgroups. The synthetic routes have the advantage of retaining chemical functionality without the side effects that come from added materials such as undesired side reactions, impurities, or miscibility issues. However, it can be difficult, time consuming, and costly to incorporate extra synthetic

steps to form various precursors. In some cases the desired properties cannot be obtained through functionality alone, in which case the use of additives becomes important.

Table 1 displays the modulus, surface tension, and theoretical resolution for several PFPE based mold materials used in this study, with PDMS values shown as a reference. The addition of a small percentage of trimethylolpropyl triacrylate (TMPTA, Figure 1) with a molecular weight of 296 g/mol to the 1.4 kg/mol PFPE-DMA resulted in an increased modulus relative to the native 1.4 kg/mol PFPE-DMA. Adding 10 wt.% TMPTA to the 1.4 kg/mol PFPE-DMA results in a modulus of 84 MPa, while further increasing the amount of TMPTA to 20 wt.% results in an even higher modulus of 96 MPa. Since increasing the modulus results in a higher resolution molding material, adding TMPTA to the 1.4K PFPE-TMA should have a beneficial effect on the mold resolution. However, the surface tension also significantly increases as more of the polar, methacrylate moeties are incorporated into the 1.4K PFPE polymer matrix. When 10% TMPTA is incorporated into the 1.4K PFPE-DMA, the surface tension increases from ~18.5 mN/m to ~23 mN/m. Upon further addition of TMPTA, the blend becomes phase separated and the surface tension increases slightly to ~ 24 mN/m. Theoretically, a negligible difference in resolution between the native 1.4K PFPE-DMA (0.39 nm) and the TMPTA/PFPE blends (0.32 nm) is expected due to the large increase in surface tension, which offsets the modulus increase.

The reason for the large standard deviation (4.3 mN/m) in surface tension for the 80:20 1.4K PFPE-DMA/TMPTA is due to microphase separation. The TMPTA material is not miscible with the 1.4 kg/mol PFPE only at 20 wt.%, at room temperature. The

miscibility of PFPE-DMA with PEG-DMA-based systems has been previously reported.³⁴





Hu et al. have previously reported the development of a series of methacrylate end-functionalized PFPE's with varying molecular masses between crosslinks (M_c) for anti-fouling applications.³⁵ The data in Table 1 illustrates how decreasing the molecular weight between the PFPE-DMA crosslinks results in an increased modulus. The three PFPE-DMA's shown in Table 1 have molecular weights of ca. 4,000 (4K), 1,400 (1.4K),

and 1,000 (1K) g/mol which correspond to modulus values of 7, 48 and 90 MPa respectively. The trend between modulus and M_c for the PFPE-DMA is not directly linear because the modulus of a rubber is also dependent upon other factors such as the volume fraction of the crosslinked chains, the firmness of chain crosslink entangling in the network, and molecular entanglements.⁷

As expected, the surface tension of the elastomer decreases as the M_c increases for the PFPE materials tested. The surface tension values increase from ~16 to ~18 mN/m when the M_c is decreased from 4K to 1K. The 1.4K and 1K PFPE-DMA's values fall within the standard deviation of each other, due to their similar molar masses. The increased surface tension is due to the increasing density of methacrylate crosslinking groups on the surface of the mold. Considering that molds for patterning applications will be fabricated from patterned silicon substrates, the surface tension of the substrate interface side of the elastomer is the most relevant value. It should be noted that the airinterface values of the elastomers are also dependant upon M_c and functionality, but have a lower absolute value than the surface side.³⁵

Increasing the functionality of the PFPE prepolymer from F = 2 to F = 4 results in a significantly higher modulus PFPE-based elastomer. Even though the molecular weight of ~2,000 g/mol for the tetrafunctional PFPE-TMA is higher than the 1,000 and 1,400 g/mol difunctional PFPE-DMA, the PFPE-TMA has a larger modulus value of 155 MPa. By increasing the functionality of the PFPE precursor materials, the modulus can be significantly increased. The surface tension of ~23 mN/m for the 2K PFPE-TMA is larger than the PFPE-DMA counterparts due to the increased density of methacrylate crosslinking groups. In terms of the theoretical resolution limit, the dramatic increase in modulus outweighs the slight increase in surface tension. The 2K-PFPE-TMA material should be the highest resolution mold material due to the high modulus and somewhat low surface tension. For these reasons, increasing functionality is an attractive route to making higher fidelity mold materials.

Using modulus (E) and surface tension (γ) values, the theoretical resolution of the mold material can be approximated by γ /E.³ Below these length scales, surface tension will prevail over elastic energy and the features will not be resolved. However, this does not seem to be an effective determinate of resolution for sub-nanometer length scales because the calculated value becomes on the order of the chemical bonds of the polymer (C-C bond ~ 0.15 nm). In addition to the properties of the mold/stamp material, there exists many other factors that can influence the pattern transfer fidelity such as feature size, aspect ratio, pattern density, sidewall profile, and processing conditions.³⁰ Previous work on replicating small nanostructures has focused on the more fundamental question of physical size limitations by replicating isolated features from master templates whose practicality is limited.⁶ A more relevant appraisal of mold resolution must be determined experimentally, with features that contain relatively moderate to high areal densities, and sub-50 nm spacing.

Material	Modulus, E, (MPa)	Surface Tension, γ, (mN/m)	Resolution, γ/E , (nm)
4K PFPE-DMA	7.0 ± 0.3^{31}	16.0 ± 0.6	2.3 ± 0.1
1.4K PFPE-DMA	48 ± 4	18.5 ± 1.2	0.39 ± 0.04
90:10 1.4K PFPE-DMA/TMPTA	84 ± 5	23.4 ± 0.9	0.32 ± 0.02
80:20 1.4K PFPE-DMA/TMPTA	96 ± 6	24.2 ± 4.3	0.32 ± 0.05
1K PFPE-DMA	90 ± 10	18.1 ± 0.7	0.20 ± 0.02
2K PFPE-TMA	155 ± 6^{31}	23.6 ± 1.2	0.13 ± 0.01
PDMS (Sylgard 184) ¹⁰	2.0	~25	~11.0
h-PDMS ⁷	~9	22 - 25	~1 - 2

Table 4.1 Modulus and surface tension values for various PFPE-based elastomers usedin this study. PDMS values are given as a reference.

4.3.2 Replication of High Arial Density, Sub-20nm Features

Shown in Figure 2 are conical silicon nanostructures with dimensions of 20 nm diameter by 40 nm height arranged in a hexagonally close-packed arrangement with a nearest neighbor spacing of 20 nm. The master has short range order but no long range order; pattern defects are present throughout and can be visualized in the SEMs shown in Figure 4.2. The features were formed using block copolymer lithography over full wafer sizes. Hard master templates with features this small, in an ordered array, over such large areas have only been realized recently due to technological breakthroughs in block copolymer lithography.^{36,37}

Master templates fabricated by block copolymer lithography provide a benchmark to probe replication processes at high feature densities over large areas not accessible by any other lithographic technique. The feature areal density of the structures shown in Figure 2 is ~500Gdot/in² with ~20nm diameter features formed over full-wafer areas. Such high density of nanometer-scale features makes these structures extremely practical for determining resolution limits of mold materials.



Figure 4.2 (A) Schematic representation of unit cell for the master template pattern and (B) schematic drawing of the cross-sectional dimensions (C) top-down and (D) 45° SEM image of master template. Scale bars are 100 nm.

Figure 4.3 shows that the fidelity of the low modulus 4K PFPE mold material is not sufficient for the replication of such small, highly dense, sharp nanostructures. Considering that the resolution of the 4K PFPE is estimated to be approximately 3 nm, it would be expected that the mold would replicate the 20 nm structures with high fidelity; however, as Figure 4.3 indicates the 4K PFPE mold clearly cannot replicate the features under common processing conditions. The replicated photoresist pattern shows a rounding of the nanostructures which is indicative of pattern deformation due to the surface tension of the mold.¹⁰ These results indicate that the resolution of the PFPE-based mold materials used in this study is not the only limiting factor in determining the

limiting size for pattern replication. The replication process was tested with the patterned side of the mold both facing up and facing down with identical results, ruling out mold orientation and gravitational forces as potential sources of the rounding effect.



Figure 4.3 Silicon master replication attempt using the low-modulus, low-surface energy 4K PFPE mold material.

In order to increase resolution yet retain mold flexibility and integrity, composite molds were fabricated according the schematic shown in Figure 4.4. Composite molds provide the benefits of both a hard rigid material for high resolution and a soft flexible material for conformable contact without applied pressure. A thin layer of one of the higher modulus PFPE's from Table 1 was used as the patterning layer with a flexible backing. The backing used was either a thick layer of low modulus 4K PFPE or a thin, flexible, polyethylene terephthalate (PET) sheet. The flexible backing layer also provides mechanical integrity so that the molds can be easily handled. The use of an inexpensive PET sheet as the backing results in an economically viable mold due the low amount of PFPE-precursor used (~100 μ L for 8 in.²).



Figure 4.4 Schematic of composite mold fabrication process; (A) a thin layer of high modulus PFPE precursor (dark green) is formed over the nanostructures of the master template, (B) a transparent flexible backing is applied and the material is cured with UV radiation ($\lambda = 365$ nm) (C) the mold is peeled off of the master and features can be formed either by traditional imprint techniques (D - F) or controlled filling (D' - F') yielding either (G) nanopatterned features in a flash layer or (H) features in a controlled flash layer. Scale bars are 100 nm.

The molds can be used in a traditional imprint process where heat and pressure is used to transfer a pattern into a low T_g material or pressure is used to fill the mold with a polymerizable liquid. Alternatively, a controlled fill and transfer technique can be

implemented where the flash layer is minimized without the use of pressure. For traditional imprint methods it is difficult in a typical laboratory setting to control the thickness of the underlying flash layer. Nanoimprint lithography (NIL) techniques use expensive machinery that relies on high temperatures and precise controls. The ultra flat layers must be perfectly parallel to allow for an even flash layer thickness. Using a fill and transfer technique the flash layer is easily controlled by casting a thin film via spin coating or with a Mayer rod. Optimizing these methods allows the mold to be filled with a controlled flash layer. The material to be patterned can then be cured onto the mold, and transferred to an underlying substrate via an adhesive or thermal transfer process. An alternative procedure can also be used where the material remains in liquid form and is laminated to a substrate prior to solidification.

Figure 4.5 shows how changing the active mold material of the composite mold affects the fidelity of the replication process. Patterns formed using the 1.4K PFPE-DMA mold material are not as sharp or well defined as those formed with the higher modulus 1.4K PFPE-DMA/TMPTA blend and PFPE-TMA. As in the case of the 4K PFPE-DMA replication, the resolution of the 1.4K PFPE-DMA mold is estimated to be ~0.5 nm, which indicates that the mold could easily replicate features that are an order of magnitude larger than the resolution. However, the mold has very poor fidelity with the sharp, conical nanostructures. The poor replication is not likely due to a filling problem because all of the materials have similar surface tensions. It should be noted that these patterns were formed in TMPTA. It is surprising that the 80:20 PFPE/TMPTA blended mold material is easily separated from the TMPTA patterned material. Though there exists 20 wt.% TMPTA in the mold, enough fluorinated moleties must be present to

allow for separation of the mold from the pattern. This opens up the possibility of patterning a variety of materials from one type of mold, without having to functionalize the mold. It is qualitatively difficult to distinguish the fidelity difference between the blended 80:20 1.4K PFPE-DMA/TMPTA material and the PFPE-TMA, as they both have similar performances. The replicated TMPTA features do not appear to be as sharp as the original silicon features. This is attributed to the 2 - 5 nm Au/Pd coating necessary to visualize the structures in SEM.



Figure 4.5 TMPTA patterns formed using a composite mold where the patterned layer of the mold was (left) 1.4K PFPE (middle) 80:20 1.4K PFPE/TMPTA blend and (right) PFPE-TMA.

Figure 4.6 shows 1K PFPE-DMA and 2K PFPE-TMA molds made from a Silicon master template that contains lines of various periodicities and spacings (additional materials are shown in supporting information). Relative to the master template, the line and spacing distances will be inverted in the PFPE molds. For example, in the Silicon master, the 150 nm period grating contains lines with a spacing of 70 nm and a width of 80 nm. Therefore, the molds of the 150 nm period grating contain lines with a spacing of 80 nm and a width of 70 nm. From figure 4.6 it is evident that both mold materials are stable for the 150 and 170 nm grating structures. For all of the ~100 nm gratings, both materials undergo significant line collapse due to the close feature spacing. At a periodicity of 120 nm, the 1K PFPE-DMA features are collapsed while the 2K PFPE-
TMA features are stable. As summarized in Table 2, these results show how the increased modulus of the 2K PFPE-TMA allows for a more stable, high resolution mold material. Though the surface tension of the mold has increased, the value of 23.6 mN/m is still an overall low value, allowing for the mold to be easily released from the master template.

4.3.3 Molding Limits: Aspect Ratio and Feature Spacing

The limiting aspect ratio before lateral collapse occurs for a square array of posts has been shown to be determined by Equation 1, where *h* is the feature height, *w* is the feature width, *d* is the feature spacing, *E* is the Young's modulus of the material, and γ_s is the surface energy.²⁹

$$\frac{h}{w} = \left(\frac{3Ew^2}{8d\gamma_s}\right)^{\frac{1}{4}} \tag{4.1}$$

To verify the validity of Equation **4.1** with the molding materials used in this study, we tested several feature sizes/aspect ratios of grating style patterns fabricated using e-beam lithography. Table 2 highlights selected results from PFPE-TMA molds of several grating structures. Using the experimentally determined surface tension value of 23.6 mN/m for the PFPE-TMA mold, the critical aspect ratio can be determined using the master dimension feature sizes. Table 2 shows that the experimental results agree well with predicted stability values. The features in the high modulus 2K PFPE-TMA molding material were stable down to linewidths of 60 nm with 60 nm spacing and an aspect ratio of 3.3. When the lines became too tall, or too closely spaced, the features

became unstable and laterally collapsed. The results are indicative of the importance of feature spacing in determining mold fidelity. Though the overall aspect ratios of the nanostructures are not very large, the close feature spacing induces collapse. A typical concern for high modulus materials is their tendency to crack and break due to their brittle nature. It is important to note that for unstable nanostructures, the low-surface energy materials do not crack or break, but can be removed from the native silicon master without any mold release layers or fluids.



Figure 4.6 SEM's of the Si grating master template and the corresponding inverse pattern in molds of 1K-PFPE-DMA and 2K-PFPE-TMA materials.

Grating Features			Stability (1K PFPE-DMA) E = 90 MPa		Stability (2K PFPE-TMA) E = 155 MPa	
70	80	200	stable	stable	stable	stable
70	100	200	stable	stable	stable	stable
60	60	200	unstable	unstable	stable	stable
60	40	200	unstable	unstable	unstable	unstable
65	40	200	unstable	unstable	unstable	unstable
65	35	200	unstable	unstable	unstable	unstable

Table 4.2 Observed vs. Predicted stability of PFPE based molds. The stability wascalculated using equation 1. The stability was analyzed via SEM.

4.3.3 Fluorinated Residue Analysis

It is well known that low molecular weight PDMS fragments adsorb onto surfaces during microcontact printing.³⁸⁻⁴⁰ The residual fragments can act as a contaminate species that hinder the functionality of the desired patterned material.³⁹ There have been several attempts to undergo cleaning procedures to remove these impurities from the original mold matrix, the most successful involving a week long cleaning procedure.³⁸ For patterns and particles fabricated with fluorinated rubbers, it is pertinent to investigate the residuals that can be transferred to surfaces. Fluorinated moieties that reside on a surface after molding or patterning with PFPE elastomers present problems for both electronic and biological applications. For electronic applications, having a –F surface can affect charge transport processes at surfaces and hinder the ability to fabricate multilayer structures as the residues tend to have a non-wetting effect. Considering the

dynamic and fragile nature of most biological processes, forming nanoparticles with undesired fluorine content could be detrimental to cellular processes. In this study we use X-ray photoelectron spectroscopy (XPS) and static contact angle measurements to determine the degree of which –F residues are present on both hydrophilic (SiO₂) and hydrophobic (SiO₂/PEG) surfaces that have come into contact with various types of PFPE-based elastomers.

Table 4.3 summarizes the XPS and H₂O static contact angle (θ_{H2O}) data shown for mold material treatment processes, mold materials, and surfaces. The contact angle of a native SiO₂ surface changes from a $\theta_{H2O} \sim 15^{\circ}$ to $\theta_{H2O} \sim 67^{\circ}$ after being in contact with a 4K PFPE DMA elastomer. XPS results show that the fluorine content also increases on the surface from <0.5 atomic %F to 17.8 atomic %F. The molds were rinsed with solkane[©] 365mfc (purchased from Solvay, 1,1,1,3,3-pentafluorobutane) prior to contact with the SiO₂ surface in an effort to wash out any unreacted oligomers or residual fluorinated moieties that may be trapped in the elastomeric matrix. Compared to the untreated mold, the treated molds decreased the contact angle of the SiO₂ substrate after contact to $\theta_{H2O} \sim 36.2^{\circ}$ for the solkane rinse and $\theta_{H2O} \sim 36.2^{\circ}$ for the vacuum treatment. Additional treatments such as solkane extraction, UVO exposure, and corona exposure were also measured qualitatively with static contact angle with results similar those reported for the solkane rinse and vacuum treatment. XPS results show that both treated samples contained similar atomic %F as the control untreated sample. These results indicate that trying to process the residuals out of the elastomer after curing is unsuccessful in removing fluorinated residuals from adsorbing onto a SiO₂ surface.

In order to compare how the crosslink density of PFPE-based elastomers affects the amount of residue left on a surface, we analyzed PFPE's with different molar masses and functionalities as shown in Table 4.3. Contact angle and XPS data show that as the crosslink density is increased, the amount of –F surface residuals is decreased. When comparing samples on a more hydrophobic PEG functionalized surface the molecular weight trend is not as clear. This is due to the 1.4K PFPE material, which shows extremely high %F and contact angle relative to the other samples. The general trend still exists with the 1K PFPE DMA and 2K PFPE TMA samples showing much less %F signal and lower contact angle values than the 1.4K PFPE DMA and 4K PFPE DMA samples. Another important trend is the reduction in residual material when the surface is changed from SiO₂ to a PEG functionalized surface. The increase in hydrophobicity causes a significant decrease in %F and $\theta_{H=0}$ for the 4K PFPE DMA, 1K PFPE DMA, and 2K PFPE TMA materials.

The results indicate that the -F moieties or residuals adsorbing onto the surfaces are hydrophobic in nature. Both the SiO₂ and PEG surfaces increase in contact angle after coming into contact with the fluorinated moieties. As the surface hydrophobicity is increased, less residual is adsorbed. This is another indication of the residuals being hydrophobic in nature, as hydrophilic surfaces usually adsorb hydrophobic materials moreso than hydrophobic surfaces. In addition, the mold materials used were hydrophobic, and most fluorinated materials are hydrophobic in nature. In order to minimize the amount of fluorine residual accumulating on surfaces, it is suggested to use hydrophobic materials and molds with high crosslink densities.

Category	Mold Material (Treatment)	Surface	%F	Static H ₂ O (θ°)	$\Delta^{o} \; (\theta_{\text{Sample}} \; \text{-} \; \theta_{\text{Sub.}})$
Control	None	SiO ₂	< 0.5	14.5 ± 0.7	N/A
	4K PFPE DMA (None)	SiO_2	17.8	67.1 ± 1.2	52.6
Mold Treatments	4K PFPE DMA (solkane rinse)	SiO_2	16.3	36.2 ± 1.0	21.7
	4K PFPE DMA (vacuum)	SiO_2	17.3	32.4 ± 0.2	17.9
Mold	1.4K PFPE DMA	SiO ₂	9.3	62.5 ± 6.2	48.0
Crosslink	1K PFPE DMA	SiO_2	1.7	23.7 ± 2.2	9.2
Density	2K PFPE TMA	SiO ₂	2.1	-	-
	None	SiO ₂ /PEG	< 0.2	39.9 ± 0.3	N/A
	4K PFPE DMA	SiO ₂ /PEG	3.4	41.8 ± 0.1	1.9
PEG Surface	1.4K PFPE DMA	SiO ₂ /PEG	7.1	43.4 ± 0.1	13.5
	1K PFPE DMA	SiO ₂ /PEG	0.4	41.1 ± 0.2	1.1
	2K PFPE TMA	SiO ₂ /PEG	0.4	45.5 ± 0.7	5.6

Table 4.3 X-ray photoelectron spectroscopy (XPS) in atomic concentration %F and static water contact angle of SiO_2 and PEG functionalized surfaces that have come into contact with PFPE molds.

4.4 Conclusion

In summary, we have shown that the modulus of PFPE based elastomers can be increased while retaining low surface energies by changing the molecular weight of the macromonomer, increasing the functionality of the macromonomer, or adding an appropriate amount of small molecule crosslinkers. For the PFPE based molds used in this study, traditional estimates of resolution (E/γ) do not correlate to pattern fidelity for replica molding of closely spaced, high density nanostructures. By using a composite mold approach, high resolution molds were fabricated out of PFPE-TMA that allowed for replication of 20 nm features with sub-20 nm spacing. Both theoretical and experimental results show that the mechanism of failure for grating style patterns is spacing dependant lateral collapse for sub-100 nm lines. Stable PFPE-TMA molds were formed from nano-

grating masters without tear-out or cracking damage that typically occurs with high modulus molds. In addition, it was found that PFPE materials with higher crosslink densities leave less residual fluorine on surfaces after contact. Evidence suggest that the fluorinated residues are hydrophobic, and their accumulation on a surface is dependent upon the surface material.

4.5 References

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Chapter 5

Recommendation for Future Directions

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5.1 Introduction

PRINT is a unique platform technology that allows for the fabrication of both isolated nanoparticles and ordered nanostructures from a variety of materials. In an effort to improve the performance of photovoltaic devices, PRINT has been utilized in two distinct size regimes: the sub 100 nm length scale used for increased exciton harvesting; and the 200 nm length scale used for increased light absorption. Future work for phototovoltaic and photonic applications based on results found in the previous chapters will be discussed.

5.2 Discussion

5.2.1 Patterning the Ideal Bulk Heterojunction

Improvements in materials and in device designs have lead to power conversion efficiencies up to 7.4 % for solid state polymer photovoltaic devices.^{1,2} Though these results are significant and record-breaking, efficiencies remain prohibitively low for commercial exploitation. Further improvements are required before this potential can be realized. As such, there is much research involved in understanding the limiting mechanism of OPV based solar cells in order to overcome current efficiency barriers.³⁻⁶

It is experimentally difficult to determine which role precisely is the limiting process that affects the overall efficiency of an OPV device. Geminate recombination, bimolecular recombination, space-charge effects, charge mobility, and light absorption are a few examples of limiting processes. Currently, the mechanism by which polymer morphology affects these processes and overall device performance in OPV cells is poorly understood.⁷⁻¹⁰ There have been several theoretical and experimental studies that take aim at showing the relationship between morphology and overall device performance.¹¹⁻¹⁴ One particularly attractive study by Marsh et al. uses a monte carlo approach to study the morphology dependence of charge carrier collection efficiency.¹⁵ Figure 5.1 shows the morphologies studied by Marsh et al. and displays disordered morphologies of intermixed donor acceptor materials with varying grain coarseness (a-d). Their model predicts that coarser blends (i.e. blends with large phase separated domains) will create isolated islands of material that will hinder charge collection efficiencies, and therefore device performance. An ideal interdigitated structure such as that shown in Figure 5.1e could achieve overall efficiencies twice as high as blends. The interdigitated structure (Figure 5.1e) consists of square columns of polymer that are 17 nm x 17 nm and 50 nm in height, with a 10 nm 'flash' layer. The electron accepting material would have to fill this nanostructure perfectly, thus forming the same dimensions as the polymer phase and containing a 10 nm 'capping' layer above the polymer structures.



Figure 5.1 Different PV active layer morphologies investigated by Marsh et. al., with dimensions given in nm: (a-d) four blends of varying coarseness, with characteristic feature sizes of 2.5, 3.0, 4.3, and 5.8 nm, respectively; (e) an idealized interdigitated morphology, consisting of interpenetrating pure columns of polymer 17 nm in width with a 10 nm capping layer at top and bottom, analogous to the ordered structure investigated by Watkins et al.¹⁶ and (f) a bilayer. (reprinted with permission from reference 15. Copyright © 2007 American Institute of Physics)

The nanostructure proposed by Greenham and co workers is similar to that proposed in another study by Watkins, which predicts an idealized interdigitated 'checkerboard' morphology, shown in Figure 5.2.¹⁶ According to their theoretical study, a maximum internalized quantum efficiency (IQE) is achieved when the widths of the 90 nm height square posts are 15 nm. The peak IQE is predicted to be approximately 1.5 times higher for the interdigitated structure compared to a disordered morphology.



Figure 5.2 Idealized interdigitated donor/acceptor 'checkerboard' morphology predicted by Watkins et al. to have 1.5 times higher IQE than a disordered morphology. (reprinted with permission from reference 16. Copyright © 2005 American Chemical Society)

There has been much interest in patterning materials for OPV devices using NIL and other methods in an effort to construct the 'ideal' interdigitated morphology.¹⁷⁻²¹ As yet efficiencies of patterned devices have remained low compared to bulk-heterojunction solution processed devices. NIL is limited as a nanofabrication technique with issues including difficulty in forming a uniform flash layer over large areas, pattern density variations, and scalability.

PRINT has been used to successfully fabricate sub 100 nm nanostructures out of anatase TiO_2 that show an increase relative to bilayer nanostructures for PV devices.²² Extending the use of PRINT for patterning titania from current results posted in chapter 3 involves the fabrication of a master template with smaller feature sizes, a higher degree of order, and controlled feature aspect ratios using block copolymer lithography. However, new challenges were encountered when using this master template for pattern replication in titania. Specifically, the height of the amorphous titania patterns did not match the original master template. Characterization of the PFPE molds indicated that they replicate the master template with a high degree of fidelity. We suspect that the titania sol-gel did not fill the PFPE mold or that it is damaged when the mold is pulled away. Reformulating the sol-gel may solve these problems. Additional improvements

could be made for TiO_2 polymer devices by employing new low-bandgap polymers that have recently shown better photovoltaic performance than P3HT. Once these challenges have been overcome, ordered BHJ photovoltaic devices with patterns closer to the ideal excitonic length scale can be fabricated and tested.

While PRINT technology provides a possible route to the formation of polymeric materials in desired morphologies, several challenges remain. A robust master template with desired dimensions and new PFPE-based molding materials that can successfully replicate those dimensions are required. Issues with fluorinated residues also must be resolved. The use of silicon nanostructures fabricated using block copolymer lithography (shown in Figure 5.1e and 5.2) as master templates is an example of structures that approach the desired morphology for ordered bulk heterojunction architecture. Silicon templates formed via block copolymer lithography have been used in a nanoimprint process as the mold material to pattern 15 nm diameter posts in P3HT.²³

Previous work has focused on developing the PRINT process to mold and replicate high area density features with novel mold formulations that exhibit little residual fluorine contamination. The materials and trends discussed in Chapter 4 should be helpful towards the development of a route to patterning OPV materials in a desired morphology on the 20 nm length scale. Purification procedures and high crosslink density molds can be utilized to minimize the amount of fluorine residuals that can contaminate a patterned polymer surface. PRINT can be used to form ideal nanostructures for OPV based devices, provided the aforementioned challenges can be met.

5.2.2 PRINT Fabricated Arrays for Increased Light Absorption

Besides an efficient hole-electron separation process, one of the foremost challenges in designing photovoltaic cells is the formation of an efficient light-trapping scheme. This is a constant challenge, regardless of employed active materials, because all the candidates have spectral absorptions that emphasize the conversion of certain wavelengths over others. For instance, traditional solar cells made of crystalline silicon (c-Si) have an indirect bandgap, which gives rise to weak absorption of light in the near infrared (near-IR).²⁴ The near-IR range of wavelengths contains 36.2% of solar photons with energies above the bandgap of c-Si. Thus, a thin c-Si solar cell with plain wafer geometry fails to absorb a significant number of photons that could otherwise be used to generate power. The same is true for all solar cells, since it is impossible to have a material with uniform coverage of the solar broad band.

The vast majority of light-trapping schemes used in solar cells today are based on geometrical optics. This approach relies in doubling the path length by a back reflector and further extension via scattering at a front surface with random texturing. Some of these light trapping schemes include collector mirrors,²⁵ microprism substrates,²⁶ and V-folded configurations.²⁷ Although most light-trapping approaches give modest enhancements, they do not have a strong impact in the cell efficiency (PCE up to 3.5 %).²⁷ Wave optics which target a specific spectral range should allow for higher performance than geometric optics based systems, which treat all wavelengths of light equally.



Figure 5.3 Schematic structure of a solar cell that is supported by a Bragg reflector as a substrate and a photonic arrangement of solar nano-converters with two periodicities Λ to optimize electron-hole capture and λ to keep the light trapped within the structure.

Photonic crystals are the best choice for a wave optics approach, because they offer complete control over the propagation of light. However, it is important to realize that photonic cell design has to combine geometric features with two length scales, a short one (~ 10 nm) consistent with the life time of the electron-hole and a long one (~ 1000 nm) on the order of the wavelength desired to be trapped. To successfully build photonic crystals for ligh harvesting, control over the spacing and disposition of nanoscale energy production centers is required. Unlike NIL, PRINT has the capability to produce structures over large areas that vary in pattern density, and contain both short and long range order. In order to significantly enhance light absorption and exciton dissociation, it would be necessary to design a master template such as that shown in Figure 5.3, which can boost the electron-hole harvest and simultaneously enhance absorption by light trapping.

To date, there have been several reports of using a wave optics approach to lighttrapping for organic solar cells. Several groups have used gratings to enhance the effective path length via diffraction.²⁸⁻³⁰ Ko et al. have already demonstrated a PRINT approach to fabricating a photoactive bulk heterojunction layer on the > 100 nm length scale.³¹ The array of posts (shown in Figure 5.4) allowed for a photonic crystal (PC) effect that led to increased light absorption for their devices. Efficiency improvements of 70% were reported due to increased light absorption and electrical enhancements. With the proper choice of periodicity and back surface omni directional reflection, this effect can be targeted to the key near-IR region of the solar spectrum and increase the interaction path by several orders of magnitude. These results are promising in that other materials can be utilized in a PC geometry that have greater absorption coefficients, charge carrier mobilities, and material compatibilities.



Figure 5.4. PC and planar geometries for organic solar cells. (a) Schematic of planar control (top) and PC (bottom) cells. (b) Planar cells (brown) and iridescent PC cells (blue) on the same device substrate. The angular dependent color from the PC cells derives from diffraction at large incident angles. (c) Scanning electron micrograph of hexagonal array of BHJ columns prior to backfilling with nc-ZnO. (d) Cross-section of PC cell showing the hierarchical arrangement of components (left without Al overcoat), right (from the top): Al/nc-ZnO/patterned TDPTD:PCBM/Flash-layer TDPTD:PCBM /PEDOT:PS/ITO/Glass. (reprinted with permission from reference 31. Copyright © 2009 American Chemical Society)

5.2.3 Potential Photonic Applications for PRINT fabricated Nanostructures

In chapter 2 it was shown that PRINT allowed for multiple patterning steps without destruction of the initial array. This ability for increased feature density by sequential patterning steps was shown to form a moiré type pattern in TiO_2 .³² Developing this process further allows for the construction of three-dimensional

nanostructures, which find utility as plasmonic crystals. A few reports exist detailing PRINT based nanofabrication methods for developing optical applications.^{33,34} Alexander et al. utilized the PRINT technique as a large area nanofabrication platform for patterning resists to create a two-dimensional array of nanoholes in a silicone substrate for surface enhanced raman scattering (SERS) applications.³³

Biosensors employ many optical based detection techniques. Methods that utilize the surface plasmon polariton (SPP) resonances have become important because they do not require fluorescence based detection protocols. SPP based methods tune device resonances to the absorption band of a molecule to be detected. There have been several reports of using soft imprint technologies to fabricate 2D metallic gratings for high performance plasmonic crystal sensors.³⁵⁻³⁷ The basic process, shown schematically in Figure 5.4, involves the fabrication of sub-micron post or hole features in an ordered array over large areas. The nanostructures are formed in a photoresist and then coated with a thin layer of gold using high vacuum deposition conditions, resulting in increased sensitivity for visible wavelengths.³⁷

The reports of soft lithography fabricated 2D photonic crystals are exciting, and open up the possibility of fabricating 2D arrays from a variety of materials using PRINT. One recent study indicates that materials other than Au may be useful for plasmonic nanocrystals.³⁸ In particular, optical devices can be fabricated from proteins or other biocompatible materials that have the concomitant effect of biological and optical function.³⁹⁻⁴¹ Using the PRINT technique, various proteins and biological materials have been formed into isolated nanoparticles while retaining functionality. By utilizing the nanofabrication techniques shown in the previous chapters to pattern solid and liquid

based solutions, PRINT is uniquely positioned to pursue photonic applications in sensors and biophotonic devices.



Figure 5.5 Schematic illustration of fabrication of nanoposts and nanopores using a PFPE/PET mold. (reprinted with permission from reference 37. Copyright © 2009 Institute of Physics Publishing Limited)

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