FABRICATION OF HIGH FIDELITY, HIGH INDEX 3D PHOTONIC CRYSTALS USING A TEMPLATING APPROACH

Yongan Xu
University of Pennsylvania, yonganxu@seas.upenn.edu

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Fabrication of High Fidelity, High Index 3D Photonic Crystals Using a Templating Approach

Abstract
In this dissertation, we demonstrate the fabrication of high fidelity 3D photonic crystal through polymer template fabrication, backfilling and template removal to obtain high index inversed inorganic photonic crystals (PCs). Along the line, we study the photoresist chemistry to minimize the shrinkage, backfilling strategies for complete infiltration, and template removal at high and low temperatures to minimize crack formation. Using multibeam interference lithography (MBIL), we fabricate diamond-like photonic structures from commercially available photoresist, SU-8, epoxy functionalized polyhedral oligomeric silsesquioxane (POSS), and narrowly distributed poly(glycidyl methacrylate)s (PGMA). The 3D structure from PGMA shows the lowest shrinkage in the [111] direction, 18%, compared to those fabricated from the SU-8 (41%) and POSS (48%) materials under the same conditions.

To fabricate a photonic crystal with large and complete photonic bandgap, it often requires backfilling of high index inorganic materials into a 3D polymer template. We have studied different backfilling methods to create three different types of high index, inorganic 3D photonic crystals. Using SU-8 structures as templates, we systematically study the electrodeposition technique to create inversed 3D titania crystals. We find that 3D SU-8 template is completely infiltrated with titania sol-gel through a two-stage process: a conformal coating of a thin layer of films occurs at the early electrodeposition stage (< 60 min), followed by bottom-up deposition. After calcination at 500 oC to remove the polymer template, inversed 3D titania crystals are obtained. The optical properties of the 3D photonic crystals characterized at various processing steps matches with the simulated photonic bandgaps (PBGs) and the SEM observation, further supporting the complete filling by the wet chemistry.

Since both PGMA and SU-8 decompose at a temperature above 400 oC, leading to the formation of defects and cracks, a highly thermal and mechanical stable template is desired for PC fabrication. We fabricate the 3D POSS structures by MBIL, which can be converted to crack-free silica-like templates over the entire sample area (~5 mm in diameter) by either thermal treatment in Ar at 500 oC or O2 plasma, and the porosity can be conveniently controlled by O2 plasma power and time. Since POSS derivatives are soluble in HF aqueous solutions, we successfully replicate the 3D porous structures into polymers, such as PGMA and poly(dimethyl siloxane) (PDMS). We note that all the fabrication processes are conducted at room temperature, including template fabrication, infiltration and removal. Further, using 3D POSS structures as templates, here, we demonstrate the synthesis of 3D photonic crystals from silicon carbide and boron carbide, respectively, which are thermally stable above 1100 oC in Ar. These non-oxide ceramic photonic crystals are potentially useful as ultrahigh temperature thermal barrier coatings that provide thermal protection for metallic components.

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FABRICATION OF HIGH FIDELITY, HIGH INDEX 3D PHOTONIC CRYSTALS USING A TEMPLATING APPROACH

Yongan Xu

A DISSERTATION

in

Materials Science and Engineering

Presented to the Faculties of the University of Pennsylvania

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Supervisor of Dissertation

Signature

Shu Yang, Associate Professor, Materials Science

Graduate Group Chairperson

Signature

Ju Li, Associate Professor, Materials Science

Dissertation Committee

Cherie R. Kagan, Associate Professor, Electrical Engineering, and Materials Science

Nader Engheta, Professor, Electrical Engineering, and Bioengineering

Roger H. French, Adjunct Professor, Materials Science
DEDICATION

This thesis is dedicated to my wife, Ling Bi, and my twins, Kayla Xu and Kelly Xu.
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ABSTRACT

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Yongan Xu

Dissertation Supervisor: Shu Yang

In this dissertation, we demonstrate the fabrication of high fidelity 3D photonic crystal through polymer template fabrication, backfilling and template removal to obtain high index inversed inorganic photonic crystals (PCs). Along the line, we study the photoresist chemistry to minimize the shrinkage, backfilling strategies for complete infiltration, and template removal at high and low temperatures to minimize crack-formation. Using multibeam interference lithography (MBIL), we fabricate diamond-like photonic structures from commercially available photoresist, SU-8, epoxy functionalized polyhedral oligomeric silsesquioxane (POSS), and narrowly distributed poly(glycidyl methacrylate)s (PGMA). The 3D structure from PGMA shows the lowest shrinkage in the [111] direction, 18%, compared to those fabricated from the SU-8 (41%) and POSS (48%) materials under the same conditions.

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study the electrodeposition technique to create inversed 3D titania crystals. We find that 3D SU-8 template is completely infiltrated with titania sol-gel through a two-stage process: a conformal coating of a thin layer of films occurs at the early electrodeposition stage (< 60 min), followed by bottom-up deposition. After calcination at 500 °C to remove the polymer template, inversed 3D titania crystals are obtained. The optical properties of the 3D photonic crystals characterized at various processing steps matches with the simulated photonic bandgaps (PBGs) and the SEM observation, further supporting the complete filling by the wet chemistry.

Since both PGMA and SU-8 decompose at a temperature above 400 °C, leading to the formation of defects and cracks, a highly thermal and mechanical stable template is desired for PC fabrication. We fabricate the 3D POSS structures by MBIL, which can be converted to crack-free silica-like templates over the entire sample area (~5 mm in diameter) by either thermal treatment in Ar at 500 °C or O2 plasma, and the porosity can be conveniently controlled by O2 plasma power and time. Since POSS derivatives are soluble in HF aqueous solutions, we successfully replicate the 3D porous structures into polymers, such as PGMA and poly(dimethyl siloxane) (PDMS). We note that all the fabrication processes are conducted at room temperature, including template fabrication, infiltration and removal. Further, using 3D POSS structures as templates, here, we demonstrate the synthesis of 3D photonic crystals from silicon carbide and boron carbide, respectively, which are thermally stable above 1100 °C in Ar. These non-oxide ceramic photonic crystals are potentially useful as ultrahigh temperature thermal barrier coatings that provide thermal protection for metallic components.
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Chapter 1

Introduction: A review of photoresist and fabrication methods for high fidelity photonic crystal

1.1 Introduction

Photonic crystals (PCs) are periodic dielectric microstructures that can manipulate the electromagnetic wave propagation. Interference of the light waves scattered from the three-dimensional (3D) photonic crystals can prohibit light propagation in any direction for a certain range of frequencies, creating a complete photonic bandgap (PBG).\(^1\)\(^2\) The PBG position and width are determined by the refractive index contrast, the structure symmetry, the lattice constant and the volume fraction of high-index materials. Because of their ability to manipulate photons on nano- and microscales, PCs offer a potential platform for the next-generation of photoelectronic devices, including micro-lasers and optics, optical circuits, optofluidic chips, high-density data storage, on-chip optical transistors and ultra-resolution sensors.\(^3\)\(^-\)\(^{13}\)

In the past two decades, many techniques have been developed for 3D nano- and microfabrications, which can be mainly categorized as bottom-up self-assembly processes and top-down lithography based techniques. Compared to self-assembly, the lithographic fabrication has advantages in terms of controlling defects and structure symmetries. There are several promising lithography techniques that have been extensively studied for mass production of 3D PCs, including phase mask interference lithography,\(^14\)\(^-\)\(^{18}\) multi-beam interference lithography,\(^4\)\(^,\)\(^19\)\(^-\)\(^{25}\) two photon lithography and
direct laser writing.\textsuperscript{26-29} However, there is no complete bandgap in the 3D structures fabricated directly by the above methods, typically from photoresists. This is because the refractive index of the photoresist materials is often low (< 1.7), whereas a minimum index contrast of 1.9 is required for a diamond structure.\textsuperscript{30} Therefore, the fabricated polymer structures have been mainly used as templates for backfilling of high refractive index materials to produce inverted 3D inorganic PCs.\textsuperscript{31}

Many backfilling techniques have been investigated to infiltrate inorganic or semiconductor materials into the polymer templates to achieve high refractive index contrast, including chemical vapor deposition (CVD),\textsuperscript{32-35} atomic layer deposition (ALD)\textsuperscript{36, 37} and electrodeposition.\textsuperscript{38-41} The infiltration/deposition of the semiconductor materials, however, are usually conducted at a temperature above 350 °C,\textsuperscript{42} where the polymer template will start to decompose and collapse, affecting the final 3D PC structures and their optical qualities. To address this problem, a double template method has been developed using a sequential SiO\textsubscript{2}/Si deposition process.\textsuperscript{35} This double templating approach will inevitably introduce more random defects into the final PCs because of the multiple steps. Therefore, it becomes increasingly urgent to design new photoresist materials and backfilling strategies to address the above problems. The ideal materials for 3D templates with high fidelity should be 1) compatible with photolithographic processes, 2) thermally and mechanically robust above 400°C, and 3) easy to remove at room temperature by either dry etching or dissolution.

Here, we summarize the recent advances in the fabrication methods for 3D polymer templates and PCs with high refractive index contrast, with emphasis on defects control
and fidelity of the 3D PC structures. An overview of the fabrication approaches for polymer templates is given in section 1.2. The photoresist chemistry is discussed in section 1.3. In section 1.4, we discuss various backfilling methods to achieve high refractive index contrast. The thesis outline is given in section 1.5.

### 1.2 Approaches to fabricate photonic crystal structures

#### 1.2.1 Block copolymer assembly

Block copolymers (BCPs) are macromolecules with sequences, or blocks, of repeating units that are chemically distinct from each other. They microphase separated into different domains to minimize the energy difference between the blocks, whose morphology is determined by the degree of polymerization (DP), volume fraction of each block, and the segment-segment interaction parameter $\chi$. At equilibrium, the BCP chains with monodisperse will arrange in the minimum free energy configurations. For an AB diblock copolymer, at least four ordered phases have been identified for different volume fractions, DP and parameter $\chi$, including lamellar, cylindrical, spherical and gyroid structures.\(^{43}\) Due to the small macromolecular domain size (10–100 nm), BCP photonic crystals are mainly of interest for applications in the visible and UV spectra.\(^{44}\)

BCP self assembly has many advantages: 1) it is a simple process driven by microphase separation, 2) the nanometer feature size can improve the performance and lower the cost of the photonic device, and 3) the photonic property can be tuned by introducing nanoparticles or by introducing a stimulus-response environment.\(^{45-49}\) However, using BCP self assembly technique, it is still difficult to pattern these
nanostructures on a large scale for practical applications, and the main challenge remains in the control of random defects, grain boundaries and orientations. This is because the thermodynamic driving forces for self-assembly are small, and low-energy defects can get easily trapped. New strategies have been explored to eliminate the defects in large area. For example, Ruiz et al. demonstrated the assembly of defect-free arrays of isolated block copolymer domains up to 100 µm X 100 µm or 3000 µm X 50 µm on chemically patterned surfaces, suitable for data storage of 1 Tb/in². This chemical patterning technique has extended the density of BCP assembled structures by a factor of four.

1.2.2 Colloidal self-assembly

Similar to BCP assembly, colloidal assembly is a simple and low-cost process to fabricate 3D PCs. The evaporation of solvent leads to the deposition of an ordered 3D packing of monodisperse particles on the substrate. The lattice parameters of the PCs can be simply tuned by changing the particle size. Most of colloidal crystals are made from sub-micrometer polystyrene (PS), poly(methyl methacrylate) (PMMA), or silica particles. The size distribution of the particles is very important to form PCs with high quality. It has been shown that there is no ordered close packing when the standard deviation of the particle diameter is above 4%.59

Compared to BCP assembly, colloidal assembly can be scaled up over several square centimeters. Many different processes have been developed for colloidal assembly, including dip-coating deposition, sedimentation, epitaxial growth on patterned substrate and spin cast. Unfortunately, the colloidal crystals formed by sedimentation
mostly are polycrystalline, containing numerous defects, such as vacancies, dislocations, stacking faults and grain boundaries. In order to increase the quality of the colloidal crystals, the external force, such as infrared-assisted heating, has been applied and the defects-free crystals with several millimeters in diameters have been obtained successfully. Recently, wafer-scale colloidal crystals have been demonstrated by simply spin coating a silica particle solution mixed with a monomer and a photoinitiator. The process can be further simplified by controlling of the volatility of the solvent. Nevertheless, it is difficult to create lattices other than face centered cubic (fcc) using colloidal assembly.

1.2.3 Two-photon lithography

In comparison to self-assembly approaches, top-down lithography methods are intrinsically free of defects. Recently, several non-conventional lithographic processes, including two-photon lithography, phase-mask interference and multibeam interference lithography, have been studied to create 3D microstructures.

In two-photon polymerization (TPP) lithography, the non-linear absorption of two photons near IR (NIR) results in photopolymerization only around the focal point. The high spatial resolution and low aspect ratio of voxels at the focal point allows for fabrication of arbitrary structures, where the size can be tuned by an appropriate laser-pulse energy and exposure time.

Despite the unique capabilities of the TPP lithography technique and its potential in microfabrications, it has not yet to be applied to industrial manufacturing. The factors
hindering the mass productions include 1) the relatively high costs of femtosecond lasers, 2) expensive positioning stage systems and optics, 3) the slow speed and small processing volume due to the serial writing process, and 4) the lack of materials with good optical and mechanical properties. Recently the processing speed has been significantly improved with the use of accurate positioning systems and fast scanners for writing of small-area structures.\textsuperscript{68}

1.2.4 Multibeam interference lithography (MBIL)

When multiple coherent beams ($n \geq 2$) impinge and focus together, the interference between $n \leq 4$ noncoplanar coherent beams gives a grating intensity distribution with $(n-1)$ dimensional periodicity. By applying this method to a photoresist film, we can create various 1D, 2D and 3D structures using so called multibeam interference lithography (MBIL) or holographic lithography (HL). It has been shown that all 14 Bravais lattices can be assembled through four-beam interference.\textsuperscript{69-72} And the interference intensity distribution is determined by the following Fourier superposition:

$$I(r) = \sum_{i=1}^{4} \sum_{m=1}^{4} \epsilon_i \epsilon_m^* \exp\left[i(k_i - k_m) \cdot r\right] \propto \left\{ \sum_{i=1}^{4} \sum_{m=1}^{4} a_{im} \exp\left[iG_{im} \cdot r\right] \right\}$$

where $k$ is the wave vector, $\epsilon$ is the polarization vector, $r$ is the position vector. $a_{im} = \epsilon_i \epsilon_m^*$ is the amplitude and $G_{im} = k_i - k_m$ is the difference between two wave vectors. $G_{im}$ determines translational symmetry, and $G_{im}$ together with $\epsilon_n$ determine the structure symmetries (i.e., space group). The lattice constants and symmetry can be controlled by the wave vectors, phase, intensity, wavelength and polarizations of the incident beams.
Figure 1.1 Schematic illustration of the fabrication process by multibeam interference lithography in a negative-tone photoresist. The post-exposure baking step was conducted under a temperature above the $T_g$ of the photoresist to allow the diffusion of the photoacids to initiate the chemical reactions.

The fabrication process by MBIL is similar to that of the conventional photolithography, including spin cast of the photoresist film, prebaking, exposure, post-exposure baking (PEB) and development processes (see Figure 1.1). The PEB is usually conducted under a temperature above the $T_g$ of the photoresist to allow for the diffusion of the photoacid upon exposure to initiate the polymerization/cross-linking (for negative-tone photoresist) or decomposition (for positive-tone photoresist) reactions, resulting in periodic 3D structures after development process. Compared to other lithography and self-assembly methods, MBIL is an efficient and promising approach for (sub)microfabrications and is robust against inevitable defects and structural deviation. It can produce defects free PCs over an area up to several square centimeters through a single exposure process, from nanoseconds to seconds. A variety of 2D and 3D structures have been demonstrated by using the MBIL technique, including biomimetic microlens, simple cubic, diamond-like and fcc structures, as well as 2D quasi-crystals.
1.2.5 Phase mask interference lithography

Compared to TPP lithography, phase mask interference lithography (PMIL) can produce 3D structures over several square centimeters in seconds. In PMIL, the photoresist film is conformably covered by a phase mask, which is usually a patterned poly(dimethylsiloxane) (PDMS).\textsuperscript{14} After exposure to a monochromatic light, the incident beam is diffracted into multiple beams, forming interference pattern in the photoresist film. Since high quality phase masks can be obtained by soft lithography replicating a master, which is defined by conventional photolithography in 2D, to PDMS, variable structures have been demonstrated by PMIL over a large area (up to 10 cm) by a single exposure.\textsuperscript{80, 81}

The 3D structures in the photoresist film are determined by the parameters of incident light and the feature of the phase mask. It remains challenging to design phase masks to obtain desirable structures due to the complexity in simulations. Further, there is no precise control of polarization in the interference pattern.

1.3 Photoresist for lithography

Different types of materials have been studied in 3D microfabrications, which can be categorized as negative-tone, positive-tone, hydrogel and hybrid photoresists, as summarized in Table 1.1.
Table 1.1 Different photoresists used in interference lithography

<table>
<thead>
<tr>
<th>Materials</th>
<th>Chemistry Structure</th>
<th>Pros</th>
<th>Cons</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative-tone</td>
<td>SU-8</td>
<td>- Thick resist</td>
<td>- Large volume shrinkage, ~42%</td>
<td>19, 83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- high resolution and contrast</td>
<td>- High refractive index</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Commercially available, and widely used for HL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PGMA</td>
<td></td>
<td>- Low volume shrinkage, ~5.9%</td>
<td>- Low refractive index</td>
<td>84</td>
</tr>
<tr>
<td>Positive-tone</td>
<td>AZ5214</td>
<td>- Low volume shrinkage</td>
<td>- Low refractive index</td>
<td>85, 86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Removable by solvent</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- High contrast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogel</td>
<td>PHEMA copolymers</td>
<td>- Biocompatible</td>
<td>- Low pattern contrast</td>
<td>87-89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Responsive</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sol-gel</td>
<td></td>
<td>- High refractive index</td>
<td>- Limited loading of metal composite</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>composites</td>
<td>- Single step fabrication</td>
<td>- Low pattern contrast</td>
<td></td>
</tr>
<tr>
<td>Hybrid</td>
<td>POSS</td>
<td>- Convertible to silica</td>
<td>- Liquid film</td>
<td>91, 92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Template for high temperature process</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hybrid</td>
<td>MSQ</td>
<td>- Convertible to silica</td>
<td>- Liquid film</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Template for high temperature process</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.3.1 Negative-tone photoresist, SU-8

Upon exposure to a light source, negative-tone photoresists will polymerize or cross-link and remain in the solvent forming negative features after the PEB and development
process (Figure 1.2). SU-8 is the most commonly used negative-tone photoresist in interference lithography. It is multifunctional epoxy derivative of a bisphenol-A novolac resin with an average of eight epoxy groups per chain. Commercial SU-8 photoresists (Microchem Inc.) contains EPON SU-8 dissolved in gamma-butyrolactone (GBL) or cyclopentanone, and a triaryl sulphonium salt as a UV photoacid generator (PAG). It is highly transparent in the near-UV and visible region, and can form thick films (~200 µm) for the fabrication of microstructures with high aspect ratios. The cross-linked SU-8 has a very high Tg (> 200 °C) and Young’s modulus (up to 5.0 GPa), therefore it has been widely used for fabrications of microelectromechanical systems (MEMS) devices, microfluidic chips and photonic crystals.

Upon exposure to visible light, the photosensitizer undergoes internal electron transfer and generates Lewis acid, which catalyzes and initiates the ring-opening polymerizations of the epoxy groups in SU-8. However, these polymerization/cross-linking reactions can form infinite polymer networks and increase the film density, therefore, cause shrinkage in the film. In addition, during development, the organic solvent would swell the crosslinked film, which further distorts the patterned film after drying. We note that the distortion caused by resist shrinkage is different from the pattern collapse caused by capillary force exerted during development, rinsing and drying steps. For the later, it can be addressed by the use of supercritical drying. A large volume of shrinkage, ~42%, has been observed in the 3D SU-8 photonic crystals after the PEB and development. This large shrinkage could cause distortion of the lattice symmetry and
periodicity from the original pattern design, thus, reducing the optical quality of the 3D photonic crystals.

**Figure 1.2** Schematic illustration of the fabrication of photonic crystals by using negative-tone and positive-tone photoresists.

Further, since SU-8 has a refractive index of ~1.6, the influence of refraction at the air/film interface cannot be ignored when the incident light travel from the air to the photoresist. To address the distortion problem, a new photoresist is desired for photonic crystal applications, which should have low refractive index and low shrinkage property. A new photoresist design will be discussed in details in Chapter 3.

**1.3.2 Positive-tone photoresist**
Upon exposure to light, acid groups in positive-tone photoresist will be deprotected, thus, dramatically changing the film polarity such that the exposed region can be removed by the aqueous base, generating positive-tone features after the PEB and development steps (Figure 1.2). Although the negative-tone photoresist can result in a thick film for template applications, it is very difficult to remove the cross-linked 3D network by either solvent or heat treatment below 400 °C. In contrast, the positive-tone photoresist can be easily removed by organic solvent, and possess very low or no shrinkage due to polarity change upon exposure to light.\textsuperscript{99,100} However, it is difficult to cast thick film from positive-tone resists and the it is especially challenging to create 3D structures from chemically amplified photoresists since photoacids can be easily consumed in the thick films.

So far, only non-chemically amplified positive-tone photoresist, AZ5214 (Clariant international Ltd.) has been demonstrated in MBIL to fabricate 3D templates. AZ5214 consists of a novolac resin as matrix and a diazonaphthoquinone as photoactive component or sensitizer. The base-insoluble diazonaphthoquinone undergoes photolysis and Wolff rearrangement to form ketene after exposure to the light source. The ketene forms a base-soluble indenecarboxylic acid in the presence of trace amount of water, which can be developed by an aqueous solution of tetramethyl ammonium hydroxide (TMAH), resulting in a positive-tone feature. The unexposed or weakly exposed region, when used as template, can be easily removed by acetone. Different groups have demonstrated the fabrication of 2D and 3D structures by using AZ5214 as photoresist,\textsuperscript{86} however, it has not been widely used for photonic crystal applications because 1)
AZ5214 has limited film thickness (< 5 µm)$^8$ and 2) strong absorption in the UV-Vis region.

1.3.3 Hydrogels

In addition to the positive-tone and negative-tone photoresists, the responsive hydrogels have drawn immense interest as tunable photonic crystals due to their large volume or lattice change under external stimuli, such as temperature, pH and humidity change. Different 3D hydrogel structures have been fabricated for applications, such as biomedical scaffolds$^{89, 101, 102}$ and gas sensors.$^{103, 104}$ Most, however, are fabricated with multiple steps, including template fabrication, back filling of the template, solidification or hardening of the hydrogel and removal of the template.$^{102-104}$ During each individual processing step, defects will be introduced that affect the fidelity of the final 3D structures.

Using poly(2-hydroxyethylmethacrylate-co-methyl methacrylate) (PHEMA-co-PMMA) (see Table 1.1) as a photosensitive precursor, Yang et al. has first demonstrated direct fabrication of 3D hydrogel through MBIL.$^8$ PMMA was used to control the content of the hydroxyl groups and avoid physical gelation of PHEMA, while PHEMA can be cross-linked by PAG and an external cross-linker (such as, tetramethoxymethyl glycoluril, TMMGU) during the PEB process. Using similar chemistry, Kang et al. fabricated 3D hydrogels using prism holography lithography.$^8$ The 3D swollen hydrogel exhibited a temperature-sensitive response, which can be explained by the viscoelastic behavior of the matrix materials upon heating, where the unit atoms of hydrogel (with a
lower T\textsubscript{g} after absorbing moisture) collapse to each other to lower the surface energy, resulting in the decrease of the lattice spacing.

1.3.4 Inorganic-organic hybrid photoresist

Holographically patterned polymer structures are often used as templates to infiltrate/deposit semiconductor or other high index materials to form photonic crystals. The infiltration/deposition of the semiconductor materials, however, are usually conducted at a temperature above 350 °C,\textsuperscript{42} where the polymer template will start to decompose and collapse, affecting the integrity of the final 3D PCs and their optical qualities. Therefore the new material/photoresist design becomes more and more important to address the above problems.

Recently, a few groups have investigated the organic/inorganic hybrids from ladder-structured methyl silsequioxane (MSQ) as precursors to fabricate thermally stable 3D structures via direct laser writing (DLW),\textsuperscript{105} or PMIL.\textsuperscript{93} The photocrosslinking of MSQ is based on the polycondensation of silanol groups to form –O-Si-O- bonds after exposure to light followed by the subsequent PEB process. The 3D organosilicate structures offer high thermal and mechanical stability, and the tempalte can be eadily removable by an aq. HF solution upon backfilling. However, the silanol groups in MSQ precursors are susceptible to temperature and environment (e.g. moisture and pH), which can cause unwanted thermal crosslinking and self-condensation in the unexposed regions. This will lower the pattern resolution and contrast, therefore, MSQ might not be compatible with MBIL technique. Based on the same chemistry as that of negative-tone SU-8 resists, we
fabricated 3D organosilicates from epoxy functionalized polyhedral oligomeric silsesquioxanes (POSS).\textsuperscript{91}

1.4 Techniques to create photonic crystals with high refractive index contrast

Table 1.2 Different processes for converting 3D polymer templates to high refractive index 3D PCs.

<table>
<thead>
<tr>
<th>Infiltration/deposition techniques</th>
<th>Pros</th>
<th>Cons</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top-down</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CVD</td>
<td>– Conformal coating&lt;br&gt;– Accurate control of filling volume fraction</td>
<td>– Incomplete filling&lt;br&gt;– High temperature process</td>
<td>25, 35, 106-108</td>
</tr>
<tr>
<td>ALD</td>
<td>– Conformal coating&lt;br&gt;– Precise control of filling volume fraction; minimum deposition thickness, 0.05 nm&lt;br&gt;– Deposition at low to intermediate temperatures</td>
<td>– Incomplete filling</td>
<td>36, 37, 109</td>
</tr>
<tr>
<td>Bottom-up</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sol-gel</td>
<td>– Wet chemical method&lt;br&gt;– Multiple infiltration cycles for complete filling</td>
<td>– Moisture sensitive&lt;br&gt;– Non-uniformity&lt;br&gt;– Large shrinkage&lt;br&gt;– Crack formation</td>
<td>4, 110-113</td>
</tr>
<tr>
<td>Electrodeposition</td>
<td>– Wet chemical method&lt;br&gt;– Complete infiltration&lt;br&gt;– High resolution, &lt; 10 nm</td>
<td>– difficult to deposit thick films</td>
<td>40, 41, 114, 115, 116</td>
</tr>
<tr>
<td>Chemical reduction</td>
<td>– One step process&lt;br&gt;– Simple and fast method&lt;br&gt;– Less defects</td>
<td>– Existence of nano pores</td>
<td>117</td>
</tr>
</tbody>
</table>
As discussed earlier, for device applications, the refractive index contrast in 3D PCs has to be high enough to open a bandgap. For example, the minimum required index contrast to open a bandgap is 1.9 for a diamond D structure. So far, many different 3D inorganic structures have been successfully fabricated based on the backfilling/infiltration of 3D colloidal assemblies and HL patterned structures, followed by removal of the template, including silicon (n = 3.45-4.20), selenium (n = 2.50), cadmium-selenium (n = 2.50-2.75), germanium (n = 4.0) and titania (n = 2.2-3.0). There are many techniques available for the backfilling or conversion of inorganic materials with high refractive index, which can be categorized as 1) top-down processes, including chemical vapor deposition (CVD) and atomic layer deposition (ALD), 2) bottom-up assemblies, including electrochemical deposition and sol-gel reactions, and 3) chemical reduction method (see Table 1.2).

1.4.1 Top-down deposition

1.4.1.1 Chemical vapor deposition (CVD)

Among all the inorganic materials with high refractive index, silicon is the most attractive because it has a relatively high refractive index, it is transparent in the near IR and IR region, and is widely used in semiconductor area. Most of the previous 3D silicon structures were fabricated by using a CVD process, a top-down process with conformal coating, and more than one complete photonic bandgaps have been observed in 3D silicon inverse opal structures.
The fabrication of a 3D silicon structure usually requires the deposition of disilane at a temperature above 400 °C,\textsuperscript{25} at which point the polymer template will decompose and collapse. Therefore a double template method is always used to convert the polymer structure into a silica template, which is thermally and mechanically stable, followed by the disilane deposition. The inverse 3D silicon structure can be obtained after selective removal of the templates, for example, by HF aq. solution etching for silica templates, and calcination or dry etching for polymer templates.

By using this method, a uniform structure can be obtained with accurate control of the film thickness. The filling-volume fraction of the dielectric materials can be tuned by changing the deposition time. Based on the Bragg’s law:

\[ \lambda = 2d_{(111)}\langle \varepsilon \rangle^{1/2} \]

where \( d_{(111)} \) is the interplanar distance along the \([111]\) direction and \( \langle \varepsilon \rangle \) is the volume averaged dielectric constant, one can easily tune the optical properties of the composite structure by control the filling volume fraction of one of the components:\textsuperscript{42}

\[ \langle \varepsilon \rangle = f_1\varepsilon_1 + f_2\varepsilon_2 \]

where \( f_1 \) and \( f_2 \) are the filling volume fractions of component 1 and 2 respectively, and \( \varepsilon_1 \) and \( \varepsilon_2 \) are the corresponding dielectric constants.

However, both experimental studies\textsuperscript{25} and calculations\textsuperscript{121} have suggested that it is nearly impossible to completely fill the holographically patterned, triply periodic bicontinuous templates through a top-down, conformal coating process. In the top-down infiltration processes, core-shell morphology is often revealed as the deposited materials
grow conformally and continuously on the 3D template surface to fill the interstitial pores. Because the pore sizes are not uniform throughout the bicontinuous template, the surface of pore network tends to pinch off (i.e., disconnects) at the narrowest pore channels before the interstitial voids are completely filled, resulting in the loss of photonic bandgap.

1.4.1.2 Atomic layer deposition

The deposition mechanism of ALD is quite similar to that of CVD, except the film is deposited with a much lower rate, 0.05 nm/cycle. The deposition of inorganic materials in ALD is based on sequential exposure to one of two complementary chemical species/precursors, which react with a surface one-at-a-time in a sequential manner. The film thickness can be precisely controlled by exposing the precursors to the growth surface repeatedly after the substrate temperature optimization.

ALD has been used to deposit conformal oxide and nitride films over a low to medium temperature range (from room temperature to 100 °C) to a precision of 0.05 nm. It has been shown that the maximum infiltration was 88% after 350 ALD cycles with a deposition rate of 0.51 Å/cycle at 100 °C.

1.4.2 Bottom-up deposition

1.4.2.1 Sol-gel reactions

Wet chemical methods could potentially offer a maximum infiltration of the 3D template structure through bottom-up assembly. In a sol-gel process, typically
the 3D template with certain functionality is immersed and filled with a metal alkoxide solution, such as the titanium (IV) isopropoxide (TIP) in isopropanol (IPA), to form a composite sol-gel thin film. Upon the subsequent calcinations, a metal oxide thin film can be formed, which thickness is dependent on the surface functionality of the substrate surface.\textsuperscript{125}

So far, many precursors have been studied and used to form inverse opal oxide structures, such as SiO\textsubscript{2},\textsuperscript{126} TiO\textsubscript{2},\textsuperscript{125} Al\textsubscript{2}O\textsubscript{3},\textsuperscript{127} and ZrO\textsubscript{2},\textsuperscript{127} by applying sol-gel reactions. The fabrication process is simple and fast, however, it is difficult to precisely control the uniformity and film thickness compared to the CVD or ALD techniques. The metal alkoxide precursors are very moisture sensitive which makes it difficult to control the degree of infiltration. Moreover, the premature condensation and cross-linking of the precursor may block the voids of the opal structure at the surface resulting in incomplete filling. It requires multiple deposition cycles to completely fill the template (Table 1.2). Further, shrinkage is a major problem during sol-gel reaction, which might cause crack and decrease the product quality.

\textbf{1.4.2.2 Electrochemical deposition}

Another wet chemical method is electrochemical deposition, which is particularly suitable for growing functional materials into complex 3D geometries. It has been commonly used in microelectronic industry, often referred to as electroplating process, to fill the deep through-holes in electrical interconnects and printed circuit boards. It possesses some unique characteristics, including 1) deposition occurs preferentially in the
bottom of the structure 2) room temperature reaction from water-based electrolytes, and
3) the ability to fill small pores (diameter ≤ 20 nm). Typically the electrodeposited
materials grow from the conductive substrate outward, leading to complete infiltration of
porous structures.

High-index inorganic materials, including CdSe, CdS, ZnO, GaAs, and TiO$_2$ have been deposited in silica colloidal templates and nanoporous channels using potentiostatic and galvanostatic deposition methods. Specifically, Miao et al. have grown TiO$_2$ nanowire arrays from anodic aluminum oxide (AAO) membranes through an electrochemically induced sol-gel reaction. The pores are nearly completely filled from the bottom to the top with very high aspect ratios (diameter as small as 10 nm and length up to 10 μm). We show in this thesis, it is possible to selectively and completely fill the titania sol-gel within the non-conductive, 3D polymer template with variable pore sizes (see Chapter 4).

1.4.3 Shape–Preserving Chemical reduction

In both the top-down or bottom-up backfilling processes, multiple steps are needed,
including the infiltration and the template removal. Recently Bao et al. have
demonstrated a magnesiothermic reduction process for converting three-dimensional
silica microshells (frustules) of diatoms (unicellular algae) into microporous
nanocrystalline silicon replicas at a temperature 650 °C. The silica diatoms were
converted into a mixture of magnesia and silicon upon exposure to the gaseous
magnesium:
\[ 2\text{Mg}(g) + \text{SiO}_2(s) \rightarrow 2\text{MgO}(s) + \text{Si}(s) \]

The formed magnesia can be etched by HCl aq. solution, thus, preserving the morphology of the 3D frustules. Therefore, it is also possible to create periodic 3D silicon photonic crystal from silica or silica-like 3D templates. However, there are always nanopores generated in the structures after HCl etching to remove the magnesia.

1.5 Current issues and thesis outline

Although a variety of photonic crystals have been fabricated by using different methods, it remains challenging to obtain high fidelity photonic crystals in large area for practical applications because of many current issues.

First of all, the polymer photonic crystals fabricated by lithography technique do not have a complete bandgap due to the low refractive index. Therefore, they are often used as templates for infiltration of inorganic materials with high refractive index, followed by removal of the template. The optical quality of the final photonic crystals will be critically determined by the fidelity of the template structures, the infiltration method, and template removal process. Most polymer templates fabricated from conventional negative tone photoresists, such as SU-8, however, always have large shrinkage due to the density change caused by cross-linking reactions. As shown in Chapter 2, we are the first to quantify the shrinkage property of 3D diamond-like SU-8 structures by MBIL, and find ~41% shrinkage in [111] direction after comparing the lattice constants obtained from SEM images with the calculated values after considering the refractive index effect. In
order to reduce the shrinkage, in Chapter 3, we design and synthesize poly(glycidyl methacrylate)s (PGMAs) with well controlled molecular weights as low-shrinkage photoresists for MBIL. A much lower shrinkage in the [111] direction, 18%, is observed from diamond-like PGMA structures in comparison to that from SU8 under the same condition, which may offer better control of the photonic bandgap properties of PCs.

The second issue is the possible incomplete infiltration. Previous study finds that backfilling of holographically patterned polymer templates, which are triply periodic bicontinuous, through top-down processes, including sequential silica/silicon CVD\textsuperscript{130} and ALD\textsuperscript{131} always results in incompletely filling. Core-shell morphology is often revealed as the deposited materials grow conformally and continuously on the 3D template surface to fill the interstitial pores. Because the pore sizes are not uniform throughout the bicontinuous template, the surface of pore network tends to pinch off (i.e., disconnect) at the narrowest pore channels before the interstitial voids are completely filled,\textsuperscript{121, 130} resulting in loss of photonic bandgap properties.\textsuperscript{121, 132} In Chapter 4, using wet chemical methods, such as electrodeposition, we obtain a nearly complete filling of the diamond-like SU-8 templates with titania, which is confirmed by comparing SEM images and FTIR reflectivity to simulation. My major contribution here is to understand how the titania sol-gel is selectively and completely filled within the 3D polymer template with variable pore sizes, and how electrochemistry occurs on a non-conductive polymer surface. By investigating the electrodeposition process step-by-step, we found that the electrodeposition in the 3D polymer templates took place in two stages. At the early stage of electrodeposition, a thin titania seed layer conformally coated on the polymer
surface. Once the metal oxide surface was established, the deposition proceeded in a bottom-up fashion. Scanning electron microscopy (SEM) images suggested a nearly completely filled 3D titania crystal without pinch-off of the pore network, which was further confirmed by reflectivity measurement of the films in the [111] direction at various processing stages in comparison to the calculated values.

Since the polymer template is highly cross-linked, it is difficult to be removed by dissolution process. However, using calcination to remove the highly cross-linked polymer template, a lot of cracks and defects are created, which are not desirable for practical devices. To address this problem, in Chapter 5, we design and fabricate 3D hybrid microstructures from photosensitive organosilicates as versatile photonic templates, such as epoxy functionalized POSS. The POSS structure can be removed conveniently by HF etching, making it attractive for low temperature process without generating cracks during the template removal process. We are the first to demonstrate templating 3D polymeric structures from PGMA and PDMS using 3D POSS structures as templates.

Lastly, the polymer templates will decompose above 500°C, making it impossible to template semiconductors (e.g. Si) and ceramics. For example, to fabricate Si photonic crystals, double templating via inverted SiO$_2$ are often used. However, more processing steps could introduce more defects in the final photonic crystals, which in turn lower the optical quality. Likewise, to template ceramic 3D photonic crystals, such as silicon carbide and boron carbide, which are of interest for thermal barrier coating, an ultrahigh processing temperature (> 1000 °C) is needed to sinter the pre-ceramic precursors. In
Chapter 5, we convert the 3D POSS structure into crack-free silica-like templates over the entire sample area (~5 mm in diameter) by either thermal treatment in Ar at 500 °C or O₂ plasma, and the porosity can be conveniently controlled by O₂ plasma power and time. Both Fourier transform infrared (FT-IR) spectroscopy and energy-dispersive X-ray (EDX) spectroscopy analysis suggest that the presence of carbon materials in the films enhance the crack-resistance of 3D POSS structures treated under Ar or oxygen plasma. The converted silica-like templates are thermally and mechanically stable, and more importantly, soluble in HF solution. In Chapter 6, we demonstrate templating of 3D SiC and BC photonic crystals the corresponding POSS structures at 1100 °C. SEM images show that ceramics nearly completely infiltrate the POSS structures. The measurement of film reflectivity in the [111] direction before and after the deposition in comparison to the calculated photonic bandgap properties suggest that the photonic structure is well-preserved at the ultrahigh temperature.

1.6 References


Chapter 2

Fabrication and characterization of 3D diamond-like SU-8 structures by MBIL

2.1 Introduction

Major progress has been made in developing different methods of fabricating 3D microstructures.\textsuperscript{1, 2} Among them, the multibeam interference lithography (MBIL) shows promise as a fast and flexible technique to create a wide range of lattices, including simple cubic,\textsuperscript{3} diamond-like,\textsuperscript{4} gyroid and face-centered cubic (fcc) structures.\textsuperscript{5, 6} Lattice constants and symmetry can be precisely controlled by the laser intensity, beam geometry, polarization and phase. During exposure, the multiple-beam interference profile is transferred to a thick photoresist film, followed by post-exposure bake and development to create the microporous structures. The resulting structure is determined by the isodose surface of the lithographic threshold value, which can be described by the corresponding level surface\textsuperscript{7}.

Many 3D photonic structures with large complete bandgaps have been proposed theoretically, while in MBIL experiments, most of the structures are fabricated from a thick negative-tone photoresist, SU-8, which has an average of eight epoxy groups per chain. Since SU-8 has a high refractive index, \textasciitilde 1.6, the influence of refraction at the air/film interface cannot be ignored when the beams travel from the air (n=1) to the resist film. To address this issue, many workers have applied prisms and/or index matching liquid\textsuperscript{4, 5, 8} to precompensate the refraction effect. However, it is difficult to completely
compensate the index mismatch due to experimental errors, and the distortion is caused by not only index mismatch but also film shrinkage, etc. Therefore, the structure distortion during MBIL and its impact on PBGs is worth to be understood quantitatively, that is, how practically theory can be used to guide experiments and optimize the optical system to give desired fabricated structures.

It is not uncommon to expect film shrinkage from the photoresists during photoexposure and development steps, especially in the case of negative-tone resists, which could further distort the fabricated structures. Campbell et al. estimated a shrinkage of 10-20% in fcc SU-8 structures fabricated by MBIL experimentally.\(^9\) Later, Meisel et al. reported 40% shrinkage in the simple cubic SU-8 structure, which completely eliminated the PBG.\(^8\) However, the shrinkage in a diamond-like SU-8 structure has not been quantitatively studied, and it is still not clear about the refraction effect on the structure distortion upon multibeam exposure.

Here, taking the diamond-like structure as a targeted example, we fabricate 3D structures from SU-8 film using four-beam interference in an umbrella configuration.\(^{10}\) We reconstruct the unit cells and level surfaces of the 3D structures in SU-8, which are then compared with those in air by considering refraction and film shrinkage separately. With the consideration of refraction only, the calculation suggests lattice stretching along the [111] direction in SU-8 film, resulting in change of translational symmetry from f.c.c. (in air) to rhombohedral (in SU-8). To quantify the shrinkage property, we compare the experimental data with the calculated values and find that there is \(~41\%\) shrinkage in the vertical direction normal to the (111) plane and a total volume shrinkage \(~42\%\) in the
whole film. Understanding the material shrinkage property and refraction effect could lead to better design of new photoresists with lower shrinkage.

2.2 Experimental methods

2.2.1 Fabrication of diamond-like SU-8 Structure

The 3D SU-8 was fabricated by exposing the spin coated polymer film, negative-tone photoresist, to four umbrella-like visible laser beams split from one coherent laser source ($\lambda=532$ nm, diode-pumped Nd:YVO$_4$ laser) following the procedure reported previously. Briefly, the central beam was circularly polarized with normal incidence to the photoresist film, while the other three surrounding beams were linearly polarized and oblique at $39^\circ$ relative to the central one. The wave vectors of four beams are $k_0=\pi/a[333]$, $k_1=\pi/a[511]$, $k_2=\pi/a[151]$, and $k_3=\pi/a[115]$, respectively. The polarization vectors of beam 1, 2, and 3 are $e_1=[-0.250 \ 0.345 \ 0.905]$, $e_2=[0.905 \ -0.250 \ 0.345]$, and $e_3=[0.345 \ 0.905 \ -0.250]$, respectively. The circular polarization of the central beam distributes the intensity equally to the surrounding beams, at a ratio of 1.8:1:1:1.

The photoresist solution (~58 wt%) was formulated by mixing Epon SU-8 pellets and 2.0 wt % Irgacure 261 (from Ciba Specialty Chemicals) as visible photoinitiators in $\gamma$-butyrolactone (GBL, Aldrich), and spin-coated on a glass substrate at 2000 rpm for 30s. To ensure good adhesion between the SU8 film and the substrate, the latter was cleaned by ultrasonication in isopropanol and acetone, respectively, followed by oxygen plasma.
The photoresist film was pre-exposure baked at 65 °C for 3 min and 95 °C for 40 min, resulting in film thickness of ~ 6 µm. The film was exposed to the superimposed interference beams (laser output of 1W) for 1-2 s. After post-exposure baking (PEB) at 65 °C for 2-4 min and 95 °C for 2-4 min, respectively, the film was developed in propylene glycol monomethyl ether acetate (PGMEA, Aldrich) to remove unexposed or weakly exposed films, resulting in 3D microporous structures. To prevent the pattern collapse of the 3D film due to the capillary force by air drying, we dried the film using supercritical CO₂ dryer (SAMDRI®-PVT-3D, tousimis) after the development.¹¹

2.2.2 Characterizations

The high resolution SEM images were taken from FEI Strata DB235 Focused Ion Beam (FIB) system at 5 kV. The lattice parameter in (111) plane was measured from the top-view SEM images by average over 2 samples at three different locations by drawing lines in three different directions. The distance between the adjacent lattice planes in the [111] direction is measured from the focus-ion-beam milled cross-section. The samples were cut by FIB normal to the surface at an acceleration current of 1000 pA. The film shrinkage was estimated by comparing the measured lattice constants from SEM with the theoretically calculated values, where the refractive index used for SU-8 is 1.6. Detailed calculation and reconstruction of the theoretical 3D structures were reported earlier.¹²

2.3 Results and discussions

To fabricate 3D photonic crystal structures, a thick photoresist film is required for multiple layers of the unit cell. Commercialized negative tone photoresist, such as SU8,
which is highly transparent in the near-UV and visible region, is often used in MBIL for 3D fabrication. During the exposure and PEB, the photoacid generators (PAGs) are activated to initiate the polymerization/cross-linking of the resist resin. The unexposed and weakly exposed regions are removed by an organic solvent, such as PGMEA, during development, resulting in porous 3D microstructures.

**Figure 2.1** SEM images of diamond-like SU-8 structures: a) large field of view, b) top view, c) cross-sectional view and d) cross-sectional view after ion milling (sample tilted at 30°).
Figure 2.1 shows the SEM images of diamond-like SU-8 structures in different views. The resulting SU-8 film is highly crosslinked and exhibits excellent thermal and high mechanical strength (Young’s modulus, E > 4.0 GPa). Upon exposure to light followed by PEB, the low-molecular weight SU-8 resin polymerizes and crosslinks into an infinite network based on a cationic ring opening reaction, leading to shrinkage in the film. While the percentage of shrinkage can be tuned by the exposure dosage, PEB time and temperature, fundamentally, the shrinkage is caused by the increase of film density during the polymerization, where the van der Waals separation of monomer units is replaced by covalent bonds.

In order to quantify the shrinkage property, we measured the lattice constants of the 3D porous SU-8 structure based on SEM images. The lattice parameter in the (111) plane was measured from the top-view SEM images by average over 2 samples at three different locations (Figure 2.1b). The distance between the adjacent lattice planes in the [111] direction was measured from the focus-ion-beam milled cross-section (Figure 2.1d). The lattice constants obtained in different directions are summarized in Table 2.1.

Since the refractive index of SU-8 is relatively high, 1.6, the refractive effect could not be ignored at the air/polymer film interface during the exposure process. Therefore we reconstructed the level surface of interference pattern in the polymer film by considering the influence of refraction at the air/photoresist film interface. Based on the reconstructed level surface, we calculated the lattice constants and found that the structure elongated in the [111] direction while almost no change in the (111) plane.
However, the shrinkage of the material will decrease the lattice constants in the [111] direction, for SU-8, it compensates the elongation caused by the refractive effect (Table 2.1). The analysis was conducted step-by-step as illustrated in Figure 2.2 and the detailed calculation and reconstruction of the theoretical 3D structures were reported in reference 12. The shrinkage of the 3D structure was then quantified by comparing the experimental data with the calculated values based on the following equation:

\[
Shrinkage\% = \frac{\text{experimental data} - \text{calculated value}}{\text{calculated value}} \times 100\%
\]

Figure 2.2 Flow chart illustrating the step-by-step theoretical analysis.
Table 2.1 Lattice parameters for the interference patterns in the air and SU8. \((c = 2\pi/d\) and \(d = 1.38\mu m)\)\(^{12}\)

<table>
<thead>
<tr>
<th>Medium</th>
<th>Air</th>
<th>SU8 (not taking into account film shrinkage)</th>
<th>SU8 (taking into account film shrinkage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reciprocal lattice vectors</td>
<td>(\vec{b}_1 = \epsilon[-1.1, 1, 1]); (\vec{b}_2 = \epsilon[1, -1, 1]); (\vec{b}_3 = \epsilon[1, 1, -1]).</td>
<td>(\vec{b}_1 = \epsilon[-1.140, 0.860, 0.860]); (\vec{b}_2 = \epsilon[0.860, -1.140, 0.860]); (\vec{b}_3 = \epsilon[0.860, 0.860, -1.140]).</td>
<td>(\vec{b}_1 = \epsilon[-1.006, 0.994, 0.994]); (\vec{b}_2 = \epsilon[0.994, -1.006, 0.994]); (\vec{b}_3 = \epsilon[0.994, 0.994, -1.006]).</td>
</tr>
<tr>
<td>Real lattice vectors</td>
<td>(\vec{a}_1 = 0.5d[0, 1, 1]); (\vec{a}_2 = 0.5d[1, 0, 1]); (\vec{a}_3 = 0.5d[1, 1, 0]).</td>
<td>(\vec{a}_1' = 0.743d[0.327, 1, 1]); (\vec{a}_2' = 0.743d[1, 0.327, 1]); (\vec{a}_3' = 0.743d[1, 1, 0.327]).</td>
<td>(\vec{a}_1'' = 0.506d[0.013, 1, 1]); (\vec{a}_2'' = 0.506d[1, 0.013, 1]); (\vec{a}_3'' = 0.506d[1, 1, 0.013]).</td>
</tr>
</tbody>
</table>

Plot of real lattices

<table>
<thead>
<tr>
<th>Translational symmetry</th>
<th>Fcc</th>
<th>Rhombohedral</th>
<th>Rhombohedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (d) ((\mu)m)</td>
<td>1.38</td>
<td>1.78</td>
<td>1.39</td>
</tr>
<tr>
<td>(</td>
<td>\vec{a}</td>
<td>) ((\mu)m)</td>
<td>0.98</td>
</tr>
<tr>
<td>Angle between (\vec{a}_i) &amp; (\vec{a}_j)</td>
<td>60°</td>
<td>38.3°</td>
<td>59.1°</td>
</tr>
<tr>
<td>Distance between the nearest lattice points in (111) plane ((\mu)m)</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>Distance between the adjacent lattice planes in [111] direction (h_{111}) ((\mu)m)</td>
<td>0.80</td>
<td>1.38</td>
<td>0.81</td>
</tr>
<tr>
<td>Space groups of the corresponding level surfaces</td>
<td>No. 166 ((\bar{R}3m))</td>
<td>No.155 ((R32))</td>
<td>No.155 ((R32))</td>
</tr>
</tbody>
</table>
Table 2.2 Shrinkage of diamond-like SU-8 structure in different lattice directions.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Pitch in the (111) plane</th>
<th>Distance between the adjacent lattice planes in the [111] direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental (µm)</td>
<td>0.97</td>
<td>0.81</td>
</tr>
<tr>
<td>Calculated* (µm)</td>
<td>0.98</td>
<td>1.38</td>
</tr>
<tr>
<td>Shrinkage (%)</td>
<td>1.0</td>
<td>41</td>
</tr>
</tbody>
</table>

*obtained from level surface by considering the influence of refraction at the photoresist film/air interface

Table 2.2 summarizes all the lattice constants obtained from both experiments and calculations. It can be seen that there is ~41% shrinkage in the [111] direction, however, there is only 1% shrinkage in the (111) plane that is parallel to the substrate surface. The total volume shrinkage is ~42% in the whole film. The difference in shrinkage in different directions can be explained by the substrate confinement effect, where the porous structure can shrink freely in the vertical direction but is restricted in the horizontal plane.\textsuperscript{12,15}

### 2.4 Conclusions

We demonstrate the fabrication of diamond-like SU-8 structures by MBIL, and quantify the shrinkage property by comparing the experimental data with the calculated values after considering the refraction effect. It has been found that there is anisotropic shrinkage in the film, that is, ~41% in the vertical direction normal to the (111) plane, and only 1% shrinkage in the (111) plane. The difference in shrinkage in different
directions is probably due to the substrate confinement effect, where the 3D structure can shrink freely in the vertical direction but is restricted in the horizontal plane. Understanding the material shrinkage property and refraction effect leads us to better design new photoresists with low shrinkage that offer high fidelity template.

2.5 References


Chapter 3

Poly(glycidyl methacrylate)s with controlled molecular weights

as low-shrinkage resins for 3D MBIL

3.1 Introduction

The commercially available negative-tone photoresist, SU-8 (Figure 3.1), has been widely used in 3D microfabrication.\(^1\) It is multifunctional epoxy derivative of a bisphenol-A novolac with an average of eight epoxy groups per chain\(^2\) and has an average molecular weight of 1397 g mol\(^{-1}\). When photoacid generators are incorporated into the SU-8 resin, these materials can be polymerized and crosslinked into an infinite network through cationic ring-opening reaction upon exposure to light. However, as discussed in Chapter 2, SU-8 templates often suffer from large volumetric shrinkage (as high as ca. 41% for a 3D diamond-like structure) after post-exposure baking (PEB) and development.\(^3\), \(^4\) While the percentage of shrinkage can be modified by the exposure dosage, and PEB time and temperature, fundamentally, the shrinkage is caused by the increase of film density during the polymerisation, in which the van der Waals separation of monomer units is replaced by covalent bonds.

One approach to address this is to design highly branched multi-functional monomers such that formation of only a few bonds can lead to a dramatic switching of solubility, thus, simultaneously improving viscosity and lowering film shrinkage. Dendrimeric methacrylates are examples of branched monomers;\(^5\) however, there is
generally a volume shrinkage of ca. 15-20% associated with the use of vinyl monomers.\textsuperscript{6} We, therefore, sought to use an epoxy-based system with a controllable number of epoxy groups in an effort to optimize the tradeoffs between solubility of our resin for good film formation and number of epoxy groups required to switch solubility.\textsuperscript{7} Glycidyl methacrylate (GMA) resins have previously been shown to form films with good mechanical properties and high chemical resistance, and have been employed for coatings, printing inks, recording materials, photoresists, and printing plates.\textsuperscript{8} Here, they were chosen as potential candidates for low-shrinkage materials and compared to that of SU-8. The molecular structures of SU-8 and GMA are illustrated in Figure 3.1.

The comparison of our experimental results with the calculated values shows that the 3D PGMA structures have a lower volumetric shrinkage, 5.9\%, than structures fabricated from SU-8 under the same conditions (42\%) in Chapter 2.

![Chemical structure of SU-8 (left) and PGMA (right)](image)

**Figure 3.1** Chemical structure of SU-8 (left) and PGMA (right)

### 3.2 Experimental methods

#### 3.2.1 Synthesis of photoresist precursors
Representative Procedure (for DP_{m}=30). Anisole (3.5 mL), freshly distilled glycidyl methacrylate (2.00 mL, 14.7 mmol), and 2-bromoproponitrile (50 µL, 0.58 mmol) were added by syringe to a mixture of CuBr (83 mg, 0.58 mmol) and 4,4'-dinonyl-2,2'-dipyridyl (600 mg, 1.46 mmol) under nitrogen at room temperature. The mixture was then heated at 60 °C under nitrogen for 12 h and then allowed to cool down to room temperature; the green solution was filtered through a silica gel plug to remove the copper-containing materials. The colorless filtrate was concentrated under reduced pressure; the residue was then dissolved in 3 mL of THF and precipitated out in ligroin to yield a white solid (1.25 g, yield: 60%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.27 (bs, 1H), 3.78 (bs, 1H), 3.20 (s, 1H), 2.81 (s, 1H), 2.60 (s, 1H), 1.93-1.86 (m, 2H), 1.30-0.60 (m, 3H) (also seen in Figure 3.1). Polymers with different degrees of polymerisation were obtained in the same way but with the following ratios of monomer:initiator: 20:1, 30:1, 35:1, 45:1, 55:1 and 105:1.

3.2.2 Fabrication of diamond-like PGMA structure

The 3D PGMA was fabricated by exposing the spin coated polymer film to four umbrella-like visible laser beams split from one coherent laser source (\(\lambda=532\)nm, diode-pumped Nd:YVO\(_4\) laser) following the procedure reported previously. Briefly, the central beam was circularly polarized with normal incidence to the photoresist film, while the other three surrounding beams were linearly polarized and oblique at 39° relative to the central one. The wave vectors of four beams are \(\mathbf{k}_0=\pi/a[3\ 3\ 3]\), \(\mathbf{k}_1=\pi/a[5\ 1\ 1]\), \(\mathbf{k}_2=\pi/a[1\ 5\ 1]\), and \(\mathbf{k}_3=\pi/a[1\ 1\ 5]\), respectively. The polarization vectors of beam 1, 2, and
3 are \( e_1 = [-0.250 \ 0.345 \ 0.905] \), \( e_2 = [0.905 \ -0.250 \ 0.345] \), and \( e_3 = [0.345 \ 0.905 \ -0.250] \), respectively. The circular polarization of the central beam distributes the intensity equally to the surrounding beams, at a ratio of 1.8:1:1:1.

The photoresist solution (ca. 27-40 wt%) was formulated in cyclohexanone (Aldrich) by mixing PGMA and 2.0 wt% Irgacure 261 ([CpFe(η^6-i-PrC_6H_5)]^+[PF_6]^-, from Ciba Specialty Chemicals) as a visible photoacid generator, and spin-coated on glass substrate at 1000-2000 rpm for 30 s.

The films were prebaked for 1 minute at 65 °C, and then exposed to the superimposed interference beams (laser output of 1 W) for 3-8 s. The power of the light source for all PGMA structures was kept as 1 W, but the exposure time was optimized to give similar porosity as those for SU-8 structures. After a post-exposure bake at 65 °C for 2-4 min and 95 °C for 1-2 min, respectively, the films were developed in propylene glycol monomethyl acetate for ca. 30-40 minutes to remove unexposed or weakly exposed films, followed by soaking in isopropanol for 5-10 minutes to obtain the 3D microporous structures. To prevent collapse of the patterned 3D film due to capillary forces upon air-drying, the films were dried using a supercritical CO_2 dryer (SAMDRI®-PVT-3D, tousimis) after the development.

### 3.2.3 Fabrication of diamond-like SU-8 structure

The 3D SU-8 structures were fabricated by using the same set-up as that for the PGMA. The photoresist solution (ca. 58 wt%) was formulated by mixing SU-8 and 2.0 wt% Irgacure 261 (from Ciba Specialty Chemicals) as visible photoinitiators in γ-
butyrolactone (Aldrich), and spin-coated on glass substrate at 2000 rpm for 30 s. The film was exposed to the superimposed interference beams (laser output of 1W) for ca. 1-2 s after soft baking. After post-exposure bake at 65 °C for 2 min and 95 °C for 2 min, respectively, the film was developed in propylene glycol monomethyl ether acetate (PGMEA, from Aldrich) to remove unexposed or weakly exposed materials, resulting in 3D microporous structures. To prevent the pattern collapse of the 3D porous film due to the capillary force during air-drying, we dried the film in a supercritical CO₂ dryer (SAMDRI-PVT-3D, tousimis) after the development.

3.2.4 Characterizations

High resolution SEM images were taken from FEI Strata DB235 Focused Ion Beam (FIB) system at 5 kV. The lattice parameter in (111) plane was measured from the top-view SEM images by average over 2 samples at three different locations by drawing lines in three different directions. The distance between the adjacent lattice planes in the [111] direction is measured from the focus-ion-beam milled cross-section. The samples were cut by FIB normal to the surface at an acceleration current of 1000 pA. The refractive indexes of the PGMA films were determined by an AutoEL-II Null Ellipsometer (Rudolph Research, Flanders NJ) at a fixed incident angle, 70°, with a Helium-Neon laser source (λ = 632.8 nm). The film shrinkage was estimated by comparing the measured lattice constants from SEM with the theoretically calculated values, where the refractive indexes, 1.60 and 1.52 were used for SU-8 and PGMA respectively. Detailed calculation and reconstruction of the theoretical 3D structures were reported earlier.¹⁰
3.2.5 Determination of epoxy cross-linking conversion

The cross-linking conversion of the epoxy groups was determined for the example with DP = 55 using IR spectroscopy (Nicolet, Nexus 470 FT-IR). The absorption at 1737 cm\(^{-1}\), assigned to the C=O stretching of the ester groups, should not change during the cross-linking, and was, therefore, used as an internal standard for quantification. The decrease of the band at 910 cm\(^{-1}\) can be attributed to the polymerization of the epoxy groups and so the conversion of the epoxy group was determined by the Beer-Lambert law from the normalized changes of absorbance at 910 cm\(^{-1}\):

\[
\alpha_{\text{epoxy}} = 1 - \frac{A'_{910}}{A^0_{910}}
\]

where \(A^0_{910}, A'_{910}\) are the normalized absorbance of the epoxy groups before and after exposure for time \(t\), respectively.\(^{11-13}\)

3.3 Results and discussions

First, we studied the influence of the degree of polymerization (DP) of the methacrylic backbone of the PGMA on the volumetric shrinkage of the diamond-like structure. Atom-transfer radical polymerisation (ATRP) has been used to obtain glycidyl methacrylate polymers with well-controlled average molecular weights and narrow molecular weight distributions.\(^{14,15}\) Accordingly, we synthesised well-defined PGMA using ATRP in anisole at 60 °C overnight, using 2-bromopropionitrile (BPN) as initiator and CuBr/dNbipy (dNbipy = 4,4'-Dinonyl-2,2'-dipyridyl) as the catalytic system (Figure
3.3) with a yield of ca. 60%. In comparison, only 50% of the monomer was polymerised after 14 hours at room temperature. The conversion was determined using $^1$H NMR spectroscopy (Figure 3.2), following the disappearance of GMA proton signals over the course of the reaction.

Figure 3.2 $^1$H NMR spectrum of poly(glycidyl methacrylate) (DP = 30) in CDCl$_3$. Note that the observed ratio of the peak areas of (a), (d) and (e) is about 3:1:, indicating that the epoxy groups in the PGMA remain intact during the polymerisation of the GMA.\textsuperscript{14}
The polymers were precipitated from ligroin as white solids and characterized by $^1$H NMR spectroscopy$^{16}$ and gel permeation chromatography (GPC). The molecular weight of the polymers was varied by using different concentrations of initiator (BPN) relative to monomer (GMA). Six PGMA samples were obtained with average DPs of 20, 30, 35, 45, 55 and 105. The polydispersity indices (PDI), obtained from GPC relative to linear polystyrene standards, are in the range of 1.21-1.39, which is similar to the literature.
value for ATRP-produced PGMA.\(^{17}\) Table 3.1 summarizes the molecular weight data for the polymers obtained from GPC in THF.

We find that the solubility of PGMA with a relatively low DP of 35 is much higher than that of PGMA with DP of 105. At a concentration of 30 wt\%, a relatively thin film (ca. 2-3 \(\mu\)m) was obtained from PGMA precursor with DP of 105, in comparison to ca. 5-6 \(\mu\)m film from DP = 35 at a concentration of 40 wt\%. To quantify the shrinkage of PGMA materials, we fabricated diamond-like structures using the same optical setup as that for SU-8 by subjecting the photoresists to four umbrella-like visible laser beams split from one coherent laser source (\(\lambda = 532\) nm, diode-pumped Nd:YVO\(_4\) laser).\(^{18}\) The films were prebaked for one minute at 65 °C, and then exposed to the superimposed interference beams (laser output of 1 W) for 3-8 s. The power of the light source for all PGMA structures was kept as 1 W, but the exposure time was optimized to give similar porosity as those for SU-8 structures.

To quantify the cross-linking conversion of the epoxy groups during the exposure and PEB process, FT-IR was used to measure the spectra of PGMA (DP = 55) after different exposure time. The absorption at 1737 cm\(^{-1}\), assigned to the C=O stretching of the ester groups, should not change during the cross-linking, and was, therefore, used as an internal standard for quantification. The decrease of the band at 910 cm\(^{-1}\) can be attributed to the polymerization of the epoxy groups and so the conversion of the epoxy group was determined by the Beer-Lambert law from the normalized changes of absorbance at 910 cm\(^{-1}\) (Figure 3.4). Our IR measurements suggest that only ca. 7-10%
epoxy groups were converted and polymerized after the PEB process. For different exposure time, the epoxy conversions are almost the same as shown in Figure 3.5.

![Absorbance vs Wavenumber graph showing FTIR spectra of PGMA (DP=55) before and after flood exposure to laser light at 1 W as the MBIL process for different period of time.](image)

**Figure 3.4** FTIR spectra of PGMA (DP=55) before and after flood exposure to laser light at 1 W as the MBIL process for different period of time.
Figure 3.5 Normalized FTIR absorbance of the epoxy group after different exposure times.

High-resolution SEM images were taken on a FEI Strata DB235 Focused Ion Beam system at 5 kV (see Figure 3.6). The pitch in the (111) plane of the 3D diamond-like structure was measured from SEM images. Each sample was measured twice in three different directions and positions, respectively. The pitch in the (111) plane of the 3D structure was measured as the average distance of center-to-center of the holes in three different directions. The distance between the adjacent lattice planes in the [111] direction was measured from the ion-milled cross-section.
Figure 3.6 SEM of diamond-like PGMA (DP=35) structures. a) Large field of view. b) Top-view. c) Cross-sectional view.

Table 3.2 Lattice parameters for the interference patterns in the air, SU-8 and PGMA. \((c = 2\pi/d \text{ and } d = 1.382\mu m.)\) (Calculated by Xuelian Zhu)

<table>
<thead>
<tr>
<th>Medium</th>
<th>Air</th>
<th>SU-8 (not taking into account of film shrinkage)</th>
<th>SU-8 (taking into account of film shrinkage)</th>
<th>PGMA (not taking into account of film shrinkage)</th>
<th>PGMA (taking into account of film shrinkage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plot of real lattices</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Translational symmetry</td>
<td>Fcc</td>
<td>Rhombohedral</td>
<td>Rhombohedral</td>
<td>Rhombohedral</td>
<td>Rhombohedral</td>
</tr>
<tr>
<td>Lattice constant (d) ((\mu m))</td>
<td>1.38</td>
<td>1.78</td>
<td>1.39</td>
<td>1.72</td>
<td>1.67</td>
</tr>
<tr>
<td>Distance between the nearest lattice</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>points in ((111)) plane ((\mu m))</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
<td>1.11</td>
</tr>
<tr>
<td>Distance between the adjacent lattice</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>planes in ([111]) direction (h_{111}) ((\mu m))</td>
<td>0.80</td>
<td>1.38</td>
<td>0.81</td>
<td>1.30</td>
<td>1.06</td>
</tr>
</tbody>
</table>
Table 3.2 summarizes the lattice parameters for the interference patterns in the air, SU-8 and PGMA. It can be seen that elongations in [111] direction are observed in both SU-8 and PGMA structures due to the refractive effect. However, this elongation or lattice distortion in PGMA structure is smaller than that in SU-8, which can be attributed to the relatively low refractive index, 1.52. The film shrinkage was estimated by comparing the measured lattice constants from SEM with the theoretically calculated values. The detailed calculation and reconstruction of the theoretical 3D structures were reported earlier.4

Table 3.3 Comparison between volumetric shrinkage of PGMA (DP=35) and SU-8 under the same fabrication conditions.

<table>
<thead>
<tr>
<th>Materials</th>
<th>PGMA (n=1.52, DP=35)</th>
<th>SU-8 (n=1.60)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pitch in the (111) plane</td>
<td>Distance between the adjacent lattice planes in the [111] direction</td>
</tr>
<tr>
<td>Experimental (μm)</td>
<td>1.05</td>
<td>1.07</td>
</tr>
<tr>
<td>Calculated* (μm)</td>
<td>0.98</td>
<td>1.30</td>
</tr>
<tr>
<td>Shrinkage (%)</td>
<td>-7.1</td>
<td>18</td>
</tr>
<tr>
<td>Volume Shrinkage (%)</td>
<td>5.9</td>
<td></td>
</tr>
</tbody>
</table>

* obtained from level surface by considering the influence of refraction at the photoresist film/air interface.

As seen from Table 3.3, the 3D structure fabricated from PGMA (DP = 35) shows much lower shrinkage (18%) in the [111] direction in comparison to that from SU-8, 41%. In the (111) plane, while the SU-8 structure was essentially unchanged,
we observed 7.1% expansion for PGMA (DP = 35). Overall, the volume shrinkage of the 3D structure is 5.9% for PGMA films, much lower than that from SU-8, 42%. For both PGMA and SU-8 templates, the difference in shrinkage in different directions can be attributed to the substrate confinement effect, where the porous structure can shrink freely in the vertical direction but is restricted in the horizontal plane.\textsuperscript{4,19}

In the case of SU-8 material, there are an average of eight epoxy groups per monomer. However, the number of epoxy groups in the PGMA precursor can be controlled by the degree of the polymerization owing to the use of ATRP. As shown in Figure 3.7, the pitch in the (111) plane increases with the DP of PGMA. Therefore, the shrinkage and periodicity of the 3D PCs can be varied to some extent by varying the molecular weight of the PGMA precursor. Compared with SU-8, the PGMA materials always show a higher pitch in the (111) plane, suggesting that PGMA exhibits lower shrinkage than SU-8 regardless of molecular weight; one of the possible factors responsible for this may be the higher flexibility of the PGMA polymer backbone. The lower shrinkage from PGMA precursors lead to larger lattice constant in the fabricated diamond-like structures, therefore, smaller lattice distortion in comparison to that of SU-8.\textsuperscript{4} Our preliminary photonic bandgap calculation suggests that the 3D PGMA structures offer better photonic bandgap quality than 3D SU-8 structures.
Figure 3.7 The pitch in the (111) plane for 3D SU-8 and PGMA structures vs. the degree of polymerizations.

3.4 Conclusions

In summary, poly(glycidyl methacrylate)s with different molecular weights have been synthesised in a well-controlled fashion using ATRP. 3D diamond-like cross-linked structures were successfully fabricated by using PGMA precursors as photoresist through the multibeam interference lithography method. The comparison of our experimental results with the calculated values showed that the 3D PGMA structures have a lower volumetric shrinkage, 5.9%, than structures fabricated from the SU-8 materials under the same conditions (42%), which may offer better control of the photonic bandgap properties of PCs templated by this material.
3. 5 References


Chapter 4

Electrodeposition of 3D titania photonic crystals from holographically patterned microporous polymer templates

In Chapters 2 and 3, we discussed the fabrication of 3D polymer photonic structures, including SU-8 and PGMA by MBIL. However, none of them can open a complete photonic bandgap due to the low refractive index of polymers, 1.4-1.6. Here, we discuss fabrication of 3D titania photonic crystals (refractive index, n=2.5) templated from the 3D polymer structures by electrodeposition method, followed by removal of the template.

4.1 Introduction

Photonic crystals with periodic modulation in refractive index or dielectric constant are of interest for numerous applications in integrated optical circuits, such as enhancing the performance of semiconductor lasers, waveguides, and all on chip optical transistors. Major progress has been made in developing different methods of fabricating 3D microstructures. However, the low refractive index of the patterned film (n < 1.7) has become the bottleneck that limits the realization of complete PBGs in the fabricated 3D crystals. The minimum required refractive index contrast to open a bandgap is 1.8 for a diamond D structure. Therefore, many begin to investigate the backfilling of high index materials, including titania (n=2.2–3.0), selenium (n=2.5), cadmium–selenium (n=2.5-
amorphous silicon (n = 3.5),\textsuperscript{7-12} and germanium (n = 4.0),\textsuperscript{13} using the fabricated 3D structures as templates. These inorganic materials can be deposited through either dry process, including chemical vapor deposition (CVD),\textsuperscript{7-12} atomic layer deposition (ALD),\textsuperscript{14, 15} and melting,\textsuperscript{5} or wet chemical methods, including liquid phase sol-gel reaction, electrochemical reaction,\textsuperscript{6} and precipitation.\textsuperscript{16, 17} Most templates studied for backfilling, however, are from closely packed colloidal crystals, which have narrow bandgaps.

Recently, triply periodic bicontinuous structures (e.g. simple cubic P, gyroid G, and diamond D), which can be patterned by holographic lithography, have received increasing interests because they possess wide, complete PBGs.\textsuperscript{3, 18, 19} The study of the backfilling of holographically patterned polymer templates through sequential silica/silicon CVD\textsuperscript{12} and ALD\textsuperscript{14} processes, however, finds it challenging to completely fill the triply periodic bicontinuous templates. In the top-down infiltration processes, core-shell morphology is often revealed as the deposited materials grow conformally and continuously on the 3D template surface to fill the interstitial pores. Because the pore sizes are not uniform throughout the bicontinuous template, the surface of pore network tends to pinch off (i.e., disconnects) at the narrowest pore channels before the interstitial voids are completely filled,\textsuperscript{12, 20} resulting in loss of photonic bandgap properties.\textsuperscript{20, 21} In contrast, wet chemical methods have been demonstrated by Meldrum \textit{et al.} to achieve maximal filling of inorganic materials,\textsuperscript{17, 22-24} including CaCO\textsubscript{3}, SrSO\textsubscript{4}, PbSO\textsubscript{4}, PbCO\textsubscript{3}, NaCl, Au, Ni and Cu, in the macroporous simple cubic polymer templates (pore size of 10-15 \textmu m), which were replicated from the sea urchin skeletal plates.
Of many wet chemical methods, electrodeposition is particularly suitable for growing functional materials into complex 3D geometries. It has been commonly used in microelectronic industry, often referred to as electroplating process, to fill the deep through-holes in electrical interconnects and printed circuit boards. It possesses some unique characteristics, including 1) deposition occurs preferentially in the bottom of the structure, 2) room temperature reaction from water-based electrolytes, and 3) the ability to fill small pores (diameter ≤ 20 nm). Typically the electrodeposited materials grow from the conductive substrate outward.

High-index inorganic materials, including CdSe, CdS, ZnO, GaAs, and TiO$_2$ have been deposited in colloidal templates and nanoporous channels using potentiostatic and galvanostatic deposition methods. Specifically, Miao et al. have grown TiO$_2$ nanowire arrays from anodic aluminum oxide (AAO) membranes through electrochemically induced sol-gel reaction. The pores are nearly completely filled from the bottom to the top with very high aspect ratios (diameter as small as 10 nm and length up to 10 µm). Using a procedure modified from Miao et al., we have shown some preliminary success to electrodeposit titania sol-gel in a holographically patterned, diamond-like polymer template. It is yet to be studied, however, whether the titania sol-gel is selectively and completely filled within the 3D polymer template with variable pore sizes, and how electrochemistry occurs on a non-conductive polymer surface. Here, we investigated the electrodeposition process step-by-step and found that the electrodeposition in the 3D polymer templates took place in two stages. At the early stage of electrodeposition (< 60 min), a thin titania seed layer (~ 55 nm) was conformally
coated on the polymer surface. Once the metal oxide surface was established, the deposition proceeded from the template bottom layer toward the top at a rate of ~0.4 μm/min. After pre-annealing the composite film at a lower temperature, 375 °C, followed by a low heating rate to 500 °C to remove the polymer template, we obtained a dense, anatase 3D titania crystal without pattern collapse. Scanning electron microscopy (SEM) images suggested a nearly completely filled 3D titania crystal without pinch-off of the pore network, which was further confirmed by reflectivity measurement of the films in the [111] direction at various processing stages in comparison to the calculated values.

4.2 Experiment methods

4.2.1 Fabrication of the diamond-like polymer templates

The 3D polymer template was fabricated by exposing the negative-tone photoresist, SU-8, to four umbrella-like visible laser beams split from one coherent laser source (λ=532nm, diode-pumped Nd:YVO₄ laser) following the procedure reported previously.¹² Briefly, the central beam was circularly polarized with normal incidence to the photoresist film, while the other three surrounding beams were linearly polarized and oblique at 39° relative to the central one. The wave vectors of four beams are $k_0=\pi/a[3 3 3]$, $k_i=\pi/a[5 1 1]$, $k_2=\pi/a[1 5 1]$, and $k_3=\pi/a[1 1 5]$, respectively. The polarization vectors of beam 1, 2, and 3 are $e_1=[-0.250 0.345 0.905]$, $e_2=[0.905 -0.250 0.345]$, and $e_3=[0.345 0.905 -0.250]$, respectively. The circular
polarization of the central beam distributes the intensity equally to the surrounding beams, at a ratio of 1.8:1:1:1.

The photoresist solution (≈ 58 wt%) was formulated by mixing Epon SU-8 pellets and 2.0 wt % Irgacure 261 (from Ciba Specialty Chemicals) as visible photoinitiators in γ-butyrolactone (GBL, Aldrich), and spin-coated on an ITO glass at 2000 rpm for 30s. To ensure good adhesion between the SU-8 film and ITO, the latter was cleaned by ultrasonication in isopropanol and acetone, respectively, followed by oxygen plasma. The photoresist film was pre-exposure bake at 65 °C for 3 min and 95 °C for 40 min, resulting in film thickness of ~ 6 µm. The film was exposed to the superimposed interference beams (laser output of 1W) for 1-2 s. After post-exposure bake (PEB) at 65 °C for 2-4 min and 95 °C for 2-4 min, respectively, the film was developed in propylene glycol monomethyl ether acetate (PGMEA, Aldrich) to remove unexposed or weakly exposed films, resulting in 3D microporous structures. To prevent the pattern collapse of the 3D film due to the capillary force by air drying, we dried the film using supercritical CO₂ dryer (SAMDRI®-PVT-3D, tousimis) after the development.³²

4.2.2 Fabrication of 3D titania photonic crystals through electrodeposition

The titania stock solution was prepared according to the procedure described in the literature.²⁶ First, the crystalline titanium powder with high purity (99.999%, Aldrich) was dissolved and oxidized in a mixture solution containing 30 vol% H₂O₂ and 30 vol% ammonia. The excess H₂O₂ and ammonia was decomposed by heating the solution to 80°C, resulting in a yellow gel. The yellow gel was then dissolved in a 4M aq. H₂SO₄ to form a red-colored stock solution for electrodeposition. Before the deposition, ~ 145 mM
potassium nitrate (KNO₃) was added in the red stock solution, and the pH of the solution was adjusted to 2-3 using the 30 vol% ammonia solution.

The electrodeposition was conducted at room temperature using a home-made three-electrode cell (Figure 4.1).³³ The deposition process was monitored using an Ag/AgCl reference electrode (Bioanalytical System Inc) with a potential range from 1.0 to 1.3 V. A Pt wire was used as the counter electrode (anode) and ITO glass as the working electrode (cathode). The current was computer controlled and maintained constant as 10 mA. The deposition rate was estimated based on SEM images at different time intervals. Since the SU-8 film was relatively hydrophobic (water contact angle ~ 80 °), we first wetted the 3D polymer template with the low surface energy solvent, methanol, before immersing the template into the titania solution. After deposition, the sample was removed from the solution and rinsed with DI water. The composite film was then calcined at 500 °C in air for ~3 hours at different heating conditions to obtain the inverse titania structures.
4.2.3 Characterization

The film thickness was measured by profilometer (Tencor Instruments, Alpha Step 10). The high resolution SEM images were taken from FEI Strata DB235 Focused Ion Beam (FIB) system at 5 kV. The powder X-ray diffraction (XRD) was performed on Rigaku Geigerflex Diffractometer using Cu as target and the two-theta angle was varied from 16 degree to 80 degree with a counting rate of 0.5 count/min. The reflectivity spectra were acquired using Varian Excalibur FTS-3000 equipped with 600 UMA microscope and Varian FTS-7000 with 600 UMA microscope, respectively. The samples were measured with the aperture size of ~100 μm x 100 μm. The photonic bandgap properties of the crystal structures obtained at different processing steps were calculated.
by MIT Photonic-Band Package, where the refractive indices of 1.6, 2.2,\textsuperscript{15} and 2.5\textsuperscript{34} were used for SU-8, amorphous titania, and anatase titania, respectively.

### 4.3 Results and discussions

Both experimental studies\textsuperscript{12, 14} and calculation\textsuperscript{20} have suggested that it is nearly impossible to completely fill the holographically patterned, triply periodic bicontinuous templates through a top-down, conformal coating process due to the pinch-off problem. Electrodeposition, however, has shown promise to nearly completely fill a three-term diamond-like polymer template with titania sol-gel.\textsuperscript{20} Questions remain how the electrodeposition occurs and evolves within the insulating 3D polymer template since the electrodeposited materials often grow from the (semi-)conductive substrate, and what is the actual filling fraction of titania within the template. In addition of SEM images, more quantitative characterization and analysis, such as reflectance measurement of the obtained 3D photonic crystals, will be necessary to reveal the nature of backfilling and the photonic bandgap properties of the film.

Our electrodeposition procedure was modified from the one demonstrated by Miao \textit{et al.},\textsuperscript{26} which grows TiO\textsubscript{2} nanowires from AAO membrane on Au substrate. The AAO and Au substrate act as the working electrodes. First, the nitrate ions are electro-reduced to generate hydroxide ions, which increase the local pH and hydrolyze the Ti precursor to form a dispersion of sol particles on the charged surface:

\[
NO_3^- + 6H_2O + 8e^- \rightarrow NH_4^+ + 9OH^- \tag{1}
\]
\[ TiO^{2+} + 2OH^- \rightarrow TiO(OH)_2(sol) \quad (2) \]

As the electrochemistry proceeds, the sol particles are crosslinked to form the titanium oxyhydroxide gel network.

\[ TiO(OH)_2(sol) - xH_2O \rightarrow TiO_{1+x}(OH)_{2-2x}(gel) \quad (3) \]

In comparison to the conventional sol-gel backfilling, this approach offers several advantages that appear attractive to completely fill the triply periodic bicontinuous structures. First, the electrochemistry generates high local pH and a pH gradient within the pore channel, leading to formation of a compact film from the template bottom up and filling small pores (diameter ≤ 20 nm). Second, the deposition thickness can be controlled by varying the deposition time and current or potential of the counter electrode. Third, the deposition rate could be manipulated by the concentration of KNO_3 solution and/or the current or potential of the counter electrode.

4.3.1 Fabrication of 3D polymer templates

The polymer template was fabricated on a conductive, transparent ITO glass substrate using 4-beam interference lithography of SU-8 film. The ITO acts as the working electrode while the transparency is important for holographic lithography, which requires minimal reflection from the substrate. To facilitate the deposition of titania sol within (sub)-micron pores while maintaining the film integrity during the electrochemical reaction, it is important to optimize the filling fraction of the porous film. As shown earlier,\textsuperscript{32} the film porosity can be varied from 10 to 80\% by changing the exposure time and intensity. Here, we first optimized the exposure time and intensity to obtain a robust
film with porosity in the range of 40-60%. We then varied the PEB time to fine-tune the filling fraction. As shown in Figure 4.2, for fixed exposure time (1-2 s) and intensity (laser output of 1W), larger porosity was obtained when PEB at 95°C for a shorter period. The film that was PEB for 2.0 min (Figure 4.2a and 4.2b) was chosen for the subsequent study of electrodeposition. The characterization of the filling fraction will be discussed later.

**Figure 4.2** SEM images of SU-8 diamond-like structures fabricated by holographic lithography with post-exposure baking (PEB) at 95 °C. a) Cross-sectional view with 2.0 min PEB time. b)-e) Top views at different PEB time: b) 2.0 min, c) 2.2 min, d) 2.5 min, and e) 2.7 min. Scale bars: 500 nm.

### 4.3.2 Mechanistic study of electrodeposition within the 3D polymer templates

It is known that the hydrolysis and gelation of sol-gels is strongly dependent on the solution pH. In our experiments, we maintained the current relatively low, 10 mA, and the concentration of KNO₃ ≤ 145 mM. At a higher KNO₃ concentration (e.g. 290 mM), a large amount of ammonia was quickly generated, resulting in immediate formation of
yellow titania gel that was broken into small pieces and floated toward the air-water interface. No deposition within the porous template was observed.

To understand the electrodeposition mechanism within the 3D polymer template, we examined the polymer/titania composite structures by SEM at different deposition time intervals. At the early deposition stage (deposition time < 60 min), a thin titania layer appeared to be conformally coated on the SU-8 template (Figure 4.3). In comparison to the polymer template (Figure 4.2a), the titania coated pore surface appeared rough and more rounded with a decreased pore size. The thickness of the titania layer was estimated ~ 55 nm at deposition time of ~ 58 min from the SEM image (Figure 4.3a vs. Figure 4.2a). The cross-sectional view (Figure 4.3c) further revealed that there was no infiltration of the titania into the bottom layers at this stage. It has been suggested that in electroplating of interconnects in integrated circuits,\textsuperscript{25} in order to coat metal or alloy over the entire surface of a patterned, insulating structure, it is first necessary to conformally deposit a seed layer, which conducts current from the electrode to the surface where a deposit is desired. Since SU-8 is non-conductive, we believe that building up a thin conformal coating of TiO\textsubscript{2} as “seed” layer on the polymer template at the initial stage is a critical step toward the subsequent electrodeposition throughout the 3D microporous template. Figure 4.3d is the schematic 2D view of the conformal coating on the template surface in the (111) plane.
Figure 4.3 (a-c) SEM images of the conformal coating of TiO$_2$ on the SU-8 template at the early deposition stage (deposition time of ~ 58 min). a) Film top layer, b) film bottom layer, and c) cross-sectional view. d) Simulated 2D view of the conformal coating in the (111) plane of the template.

Once the seed layer was established, the deposition proceeded rather quickly. The 3D SU-8 template (~ 6 μm thick) was nearly completely filled within 15 min (Figure 4.4) at a rate of ~ 0.4 μm/min in a bottom-up fashion. Figure 4.4 shows the SEM images of a free-standing TiO$_2$/SU-8 composite film up-side down. At the deposition time of ~ 60 min, the first bottom layer began to be partially infiltrated (Figure 4.4a). At ~ 65 min, the second bottom layer was filled (Figure 4.4b), and the infiltration was completed at ~ 75
min (Figure 4.4c). Since the bottom ITO substrate is more conductive than the sides of the template coated with titania, it is expected that the local current density, therefore, the concentration of OH− groups, should be much higher at the template bottom layer than that on the sidewalls (Figure 4.4d). The high local pH at the bottom layer leads to more complete hydrolysis and condensation, resulting in formation of a relatively compact film, therefore, further restricts the transport of ions to the upper layer.26 As the deposition precedes, the pH gradient increases with decrease of the pore size, causing a much higher deposition rate at the second deposition stage. The cross-sectional SEM image of the composite (Figure 4.4c) shows no obvious pinch-off of pore network in comparison to that seen in silica/SU-8 structures filled by CVD process.12, 20 For void-free filling, a higher deposition rate at the template bottom than on the sidewalls is desired,25 which can be attributed to the diffusion-controlled OH− concentration and the pH gradient. Similar strategy has been applied in damascene Cu plating25 to seamlessly deposit Cu defect-free within lithographically patterned cavities, which have vertical walls and high aspect ratios, by using additives to inhibit the transport of cupric ion, Cu2+. The deposition rate is much higher at the bottom of the feature where the diffusion-controlled inhibitor concentration is the lowest.
4.3.3 Calcinations of the composite films and film shrinkage

After the backfilling, the polymer/titania composite was calcined at 500 °C to remove the polymer template, resulting in the inverse titania photonic crystal. It is important though to pre-anneal the sample and optimize the heating rate to densify the titania gel before removal the polymer template to prevent film collapse. Here, we purposely used the titania/SU-8 composite with thin titania conformal coating (~ 55 nm, Figure 4.3a) to optimize the calcination conditions. As seen in Figure 4.5a, when the
composite was directly heated to 500 °C at a fast heating rate of 9 °C/min in air, the titania skeleton was not condensed enough to withstand the high calcination temperature, resulting in a rather porous and nearly collapsed film. In contrast, when the composite was pre-annealed at 375 °C for ~7 hrs in air, followed by a slow ramping rate (3 °C/min) to 500 °C, a rather robust and dense titania skeleton was observed (Figure 4.5b). It has the same 3D structure as the original polymer template (Figure 4.2a), which further confirms the conformal coating of titania on polymer template at the early electrodeposition stage. For the 3D titania film that was electrodeposited for ~ 79 min, followed by the two-step calcination process, we can clearly see a very dense titania film without any unfilled pore voids or nanopores (Figure 4.6).

![Figure 4.5 SEM images of inverse titania 3D skeletons obtained from electrodeposition for ~ 58 min on SU-8 template, followed by different calcination conditions: a) direct ramping to 500 °C in air at a rate of 9 °C/min without pre-annealing, b) pre-annealing at 375 °C for ~7 hrs in air, followed by heating to 500 °C at a rate of 3 °C/min and held at 500 °C for 3 hrs.](image-url)
Figure 4.6 SEM images of the inverse 3D titania crystals after pre-annealing at 375 °C and calcination at 500 °C for 3 hrs. a) Top-view, and b-c) cross-sectional views at different magnifications. The film was electrodeposited for ~79 minutes.

During pre-annealing and calcination steps, the sol-gel film is further densified, thus, large film shrinkage is often expected.\textsuperscript{36,37} Cracks will occur and propagate if the film is attached to the substrate due to the residue strain generated from the shrinkage and the mismatch of the coefficient of thermal expansion between the titania and the substrate. To quantify the shrinkage of the 3D titania film fabricated by the electrodeposition technique, which would be important to the later photonic bandgap simulation, we compared the periodicity of titania crystal with that of the SU-8 template in the (111) plane and [111] direction (see Table 4.1). The shrinkage in the (111) plane is 26.8%, whereas that in the [111] direction is 33.3% with the film attached to the substrate (Table 4.1). Typically there are areas of a few hundreds of microns wide crack-free and suitable for the optical characterization. When the film is lifted-off from the substrate before calcinations, allowing for more uniform shrinkage, a titania film with far fewer cracks can be obtained.
Table 4.1 Comparison of periodicity in the inverse 3D titania crystal with that in the SU-8 template. The titania film was pre-annealed at 375 °C for ~7 hrs in air, followed by heating to 500 °C at a rate of 3 °C/min and held at 500 °C for 3 hrs. The SU-8 films were milled by focus-ion beam (FIB) in perpendicularly to the (111) plane with an output current of 1000 pA.

<table>
<thead>
<tr>
<th>Periodicity</th>
<th>SU-8 template</th>
<th>Titania crystal</th>
<th>Film shrinkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the (111) plane (μm)</td>
<td>0.97</td>
<td>0.71</td>
<td>26.8%</td>
</tr>
<tr>
<td>In the [111] direction (μm)</td>
<td>2.43</td>
<td>1.62</td>
<td>33.3%</td>
</tr>
</tbody>
</table>

4.3.4 Crystallinity of the calcined titania

Titania could have several crystalline phases with different refractive indices, including anatase, rutile, and their mixtures. When the TiO₂ gel is sintered at 500 °C, anatase phase³⁸ is often obtained with a refractive index of 2.5,³⁹ which can be completely converted to rutile (n ~2.70-3.0) at 1000 °C. Using powder X-ray diffraction (XRD) technique, we characterized the bulk titania film deposited on the ITO glass outside of the patterned region, which was calcined at 500 °C for 3 hrs. Figure 4.7 shows peaks at 2θ =25.4°, 38.3°, 48.1°, 55.2° and 62.3°, corresponding to the different crystal planes in the anatase titania, whereas those at 2θ = 30.7°, 35.6°, 51.0° and 60.9° are assigned to the ITO glass substrate.⁴⁰
Figure 4.7 XRD diffraction pattern of the bulk titania film after calcination at 500 °C for 3 hrs. *: peaks from ITO glass substrate.

4.3.5 Optical characterization of the 3D photonic crystals

To quantitatively evaluate the completeness of the backfilling, we measured the reflectance of the photonic crystals (SU-8, SU-8/TiO₂ composite, and inverse TiO₂) obtained at different processing steps in the [111] direction, and compared them with the calculated PBG (Figure 4.8). The PBG was calculated by considering the structure distortion due to refractive effect at air-film interface and film shrinkage after lithography and calcination steps.⁴¹
In the reflectance spectrum of the SU-8 template (Figure 4.8a), the interference fringes are related to film thickness $t$ as\textsuperscript{42}:

$$t = \frac{\Delta m}{2n_{\text{eff}}(\nu_1 - \nu_2)}$$  \hspace{1cm} (4)

where $n_{\text{eff}}$ is the effective refractive index, $\Delta m$ is the number of fringes, $\nu_1$ and $\nu_2$ are the wavenumbers of different fringes. For $t = 6.0$ $\mu$m, we obtain the effective refractive index of the film, $n_{\text{SU8/air}}=1.3$. The filling volume fraction can be estimated by\textsuperscript{39}:

$$n_{\text{eff}}^2 = f_1n_1^2 + (1-f_1)n_2^2$$  \hspace{1cm} (5)

where $n_1$ and $n_2$ are the refractive index of component 1 and 2, respectively, and $f_1$ is the filling volume fraction of component 1. For $n_{\text{SU8}}=1.6$ and $n_{\text{air}}=1$, we obtain $f_{\text{SU-8}}=44\%$, which is the same as that estimated from the reconstructed 3D SU-8 structure using SEM images from different cleavage planes. There was a 10\% red shift (0.1~0.2 $\mu$m) of the experimentally observed peak position at $\lambda = 2.4$ $\mu$m with respect to the calculated PBG in the [111] direction between the 2nd and 3rd bands (Figure 4.8a). We measured the reflectance spectrum of the 3D SU-8 film from three different research groups using both Varian Excalibur FTS-3000 and Varian FTS-7000, and confirmed that the reflectance peak always appeared at 2.4 $\mu$m. We think the small discrepancy in peak location between experiment and calculation may be due to the experimental error, which could slightly shift the level surface of the fabricated 3D structure, or simply due to the non-uniform porosity caused by the Gaussian distribution of the laser intensity.\textsuperscript{12}
Figure 4.8 FTIR reflectance spectra of 3D diamond-like structures in the [111] direction: a) SU-8, b) SU-8/TiO$_2$, and c) inverse TiO$_2$. In each panel, the left figure is a simulated spectrum and the right one is the experimental data.

Compare to the SU-8 template, there was a bathochromic shift of the reflection peak to $\sim$3.2 $\mu$m in the SU-8/TiO$_2$ composite (Figure 4.8b) due to the increase of the mean dielectric field of the composite even though there is a decrease of the refractive index contrast. According to Bragg’s Law, at the normal incidence to the (111) plane the reflectance peak wavelength is

$$\lambda = 2d_{111}n_{\text{eff}}$$  \hspace{1cm} (6)

where $d_{111}$ is the interlayer distance in the [111] direction. For $d_{111} = 0.81$ $\mu$m (measured from SEM), we estimate that the effective refractive index for the composite is $n_{\text{SU8/TiO2}} \approx 2.0$, which agrees with the reported value in the literature.$^{43}$ Therefore, the refractive index of the as-deposited titania film is estimated by Eq. 5 as
$n_{\text{TiO}_2, \text{as-deposited}} = 2.2$, corresponding to that of amorphous titania. Figure 4.8b clearly shows that the reflection peak of the SU-8/TiO$_2$ structure matches well with the calculated peak position. More strikingly, the estimated volume fraction of the amorphous TiO$_2$, 56%, is the exactly same as the air volume fraction in the SU-8 template, which undoubtedly confirms that the SU-8 template is nearly completely filled by electrodeposition method.

After calcination to remove the polymer template, the reflection peak of the 3D inverse TiO$_2$ crystal blue shifted to $\sim 2.2$ µm, which agrees reasonably well with the calculated peak position assuming $f_{\text{TiO}_2, \text{anatase}} = 56\%$ (Figure 4.8c). The reflectance peak appeared rather broad though, which might be attributed to the finite size of the sample ($\sim 200$ µm) in the FTIR measurement. The peak reflectivity increased from 24% for SU-8 to 76% for inverse TiO$_2$ (anatase) photonic crystal, indicating increased optical quality of the film. From Bragg’s Law, the effective index for the inverse TiO$_2$ structure is calculated as $n_{\text{TiO}_2/\text{air}} = 2.0$. Assuming $n_{\text{TiO}_2, \text{anatase}} = 2.5$, we obtain the filling volume fraction of titania, $f_{\text{TiO}_2, \text{anatase}} = 57\%$. It again agrees well with volume fraction of the air in the SU-8 template, $f_{\text{air}} = 56\%$ (Table 4.2), further supporting the complete filling of titania sol-gel into the polymer template through the electrodeposition process. It is noted that the lattice constant of the calcined titania crystal is smaller than that of the polymer template. Therefore, the similarity between the titania filling volume fraction in the inverse titania crystal and the air volume fraction in the polymer template suggests that the 3D structure is well-preserved during the backfilling and calcination steps.
Table 4.2 Comparison of the optical properties and filling volume fractions of the 3D photonic crystals obtained at different processing steps.

<table>
<thead>
<tr>
<th>Photonic crystals</th>
<th>Reflectance peak position (μm)</th>
<th>Effective refractive index of film ($n_{\text{eff}}$)</th>
<th>Filling volume fraction Component 1</th>
<th>Component 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU-8/air</td>
<td>2.4</td>
<td>1.3</td>
<td>$f_{\text{SU8}} = 44%$</td>
<td>$f_{\text{air}} = 56%$</td>
</tr>
<tr>
<td>SU-8/TiO_2</td>
<td>3.2</td>
<td>2.0</td>
<td>$f_{\text{SU8}} = 44%$</td>
<td>$f_{\text{TiO}_2} = 56%$</td>
</tr>
<tr>
<td>air/TiO_2</td>
<td>2.2</td>
<td>2.0</td>
<td>$f_{\text{air}} = 43%$</td>
<td>$f_{\text{TiO}_2} = 57%$</td>
</tr>
</tbody>
</table>

4.4 Conclusions

We systematically studied the backfilling of the holographically patterned diamond-like polymer templates with titania sol-gel using the electrodeposition technique. The electrodeposition appeared to proceed in two stages (Figure 4.9). At the early stage of electrodeposition ($< 60$ min), a thin titania film was conformally coated on the surface of polymer template, creating a seed layer that appeared critical for further bottom up electrodeposition. In the second stage, the deposition rate on the existing titania surface increased significantly at a rate of 0.4 μm/min, and the deposition occurred preferentially from the film bottom layer, which could be attributed to the diffusion-controlled hydroxyl ion concentration and a pH gradient within the template. SEM images suggested there was no pinch-off of the pore network after the backfilling. After calcination at 500 °C to
remove the polymer template, a nearly completely filled inverse 3D titania structure was obtained. We showed that a combination of pre-annealing step and a slow heating rate was important to form a dense 3D anatase titania crystal without pattern collapse. The optical properties of the 3D photonic crystals were measured at various processing steps and compared with the PBG calculation. The nearly perfect agreement of the experimental reflectance spectra with the simulated ones, and thus the obtained volume fraction at each step strongly supported the SEM observation: i.e., the polymer template was nearly completely filled with titania by the bottom-up process. Although the study reported here focuses on electrodeposition of titania sol-gel, we believe the understanding of backfilling mechanism will offer important insights to broaden the application of templating approaches and deposition of other high index materials.

![Schematic illustration of the electrodeposition process to backfill titania sol-gel into the 3D SU-8 template.](image)

**Figure 4.9** Schematic illustration of the electrodeposition process to backfill titania sol-gel into the 3D SU-8 template.

4.5 References


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Chapter 5

Crack-free 3D hybrid microstructures from photosensitive organosilicates as versatile photonic templates

In Chapter 4, we demonstrate a nearly completely infiltrated inverse titania photonic crystals (PCs) templated from the SU-8 polymer structure. To remove the cross-linked polymer template, calcination above 400 °C in air, however, is needed to decompose the SU-8 template, creating many microcracks in the structure, which decreases the optical quality of the PCs for practical applications. Likewise, the polymer templates cannot be used for direct deposition of semiconductor materials, such as Si, which requires deposition temperature > 350 °C. A double templating process is often employed.\textsuperscript{1, 2} However, multiple templating processes could further introduce unwanted defects in the final photonic crystal structure, decreasing the optical properties. To address the concern on thermal and mechanical stability of polymer template, we investigate the fabrication of 3D photonic structures from organosilicates, which can be easily removed by acid etching or plasma etching.

5.1 Introduction

Three-dimensional (3D) structures with (sub)micron periodicity are of interest for a wide range of applications, including photonic\textsuperscript{3} and phononic crystals,\textsuperscript{4, 5} optical data
storage,\textsuperscript{6} microfluidics,\textsuperscript{7, 8} optofluidics,\textsuperscript{9} sensors,\textsuperscript{10-12} tissue scaffolds,\textsuperscript{13} as well as controlled delivery.\textsuperscript{14} Various fabrication methods, including self-assembly, standard layer-by-layer microfabrication process, and non-conventional optical lithography, have been studied to create various 3D structures with (sub)micron periodicity in a controlled manner.\textsuperscript{15-17} The requirement of photosensitive materials, however, limits direct fabrication of 3D microstructures over a wide range of materials that are not compatible with lithographic process, such as high index semiconductors for complete photonic bandgap (PBG) properties, and responsive hydrogels and elastomers for dynamic tuning of the structure- property.

Alternatively, the patterned 3D polymer structures can be used as templates for backfilling with organic, hybrid, and inorganic materials, followed by removal of the polymer template to obtain inverse 3D structures. Because the 3D polymer templates fabricated by interference lithography are bicontinuous networks, after backfilling they have to be removed either by thermal decomposition or dissolution. In interference lithography, negative-tone photoresists (e.g. SU-8) are commonly used,\textsuperscript{15, 17} which form highly crosslinked 3D networks that are difficult to remove by solvent or heat below 400°C. Therefore, it is not possible to template other organic polymers, specifically, responsive hydrogels and elastomeric poly(dimethylsiloxane) (PDMS) films, from the negative-tone resist templates. A handful of groups have used commercially available positive-tone resist, AZ5214 (Clariant International Ltd.) to create 2D and 3D structures,\textsuperscript{5, 15} which can be easily dissolved in an organic solvent after infiltration. Jang et al.
fabricated a 3D PDMS film from the corresponding AZ5214 template as a tunable phononic crystal. However, the aromatic groups in AZ-series resists are highly absorbing in the UV-vis region, thus, limiting the film thickness of 3D structures to less than 5 µm.

An ideal 3D template should be 1) compatible with photolithographic process, 2) thermally and mechanically robust above 400°C, and 3) easy to remove at room temperature by either dry etching or dissolution. Polyhedral oligomeric silsesquioxanes (POSS) are a unique class of hybrid materials, which possess the structure of cube-octameric frameworks with eight organic corner groups. They have a chemical composition of RSiO$_{1.5}$ with thermal and mechanical properties intermediate between SiO$_2$ and organic polymers. The functional groups, such as epoxy and (meth)acrylate, can be introduced to make the POSS materials photopatternable. Further, the presence of organic moieties makes POSS compatible with various polymer systems, as well as enhance crack resistance of the film.

Recently, we have investigated the direct fabrication of 3D silica-like structures from epoxy-functionalized cyclohexyl polyhedral oligomeric silsesquioxanes (epoxy POSS) using four-beam interference lithography. We showed that the 3D epoxy POSS structures were maintained without global volume shrinkage during the heat treatment (up to 400°C) by thinning the struts that connect motifs. Since organosilicates can be conveniently converted to silica by thermal decomposition of the organic moieties, which can be subsequently removed by aqueous hydrofluoric acid (HF) solution at room
temperature, the 3D POSS structures are attractive as templates for infiltration of a wide range of organic and inorganic materials. However, we found micro-cracks had appeared all over the POSS film when heating above 400°C in air due to the residue strain in the porous film caused by the large mass loss and materials shrinkage. To eliminate the cracks and maintain the high fidelity of the 3D structures, a few groups have investigated application of a sacrificial layer between the film and substrate,\textsuperscript{19, 27} such that the obtained free-standing films shrink isotropically during sintering to minimize residual strain within the film. Nevertheless, this approach is not ideal for fabrication of on-chip devices. Recently, Orilall \textit{et al.}\textsuperscript{28} have shown stable macroporous 3D structures from polystyrene colloidal templates, which were heated under inert atmosphere up to 900 °C. The stability was attributed to the formation of amorphous/graphitic-like carbon within the template.

Here, we demonstrate the fabrication of crack-free 3D silica-like structures over a large area (~ 5 mm in diameter) when treating the diamond-like epoxy POSS films in two different processes, including thermal treatment under an Ar environment and O\textsubscript{2} plasma etching. The diamond-like POSS films were fabricated through four-beam interference lithography, followed by calcinations under either an O\textsubscript{2} or Ar environment or O\textsubscript{2} plasma etching, to investigate the thermal and mechanical stability of the resulting films. The 3D structure was maintained when calcined at a temperature up to 1100°C, and crack-free samples were obtained when the POSS films were treated with a low intensity O\textsubscript{2} plasma or heated at 500°C under an Ar environment, in contrast to crack formation when heated
Fourier transform infrared (FT-IR) spectroscopy and energy-dispersive X-ray (EDX) spectroscopy analysis suggested that the chemical nature and composition of the films remained the same as POSS after O$_2$ plasma, whereas a large quantity of amorphous carbon was found in the film calcined in Ar, which might contribute to the crack-resistance of the films. In contrast, the POSS film was nearly completely converted to silica when calcined in O$_2$. Further, the volume fraction of the porous film could be conveniently controlled by O$_2$ plasma etching time and power. Since the epoxy POSS film and its derivatives could be easily removed by HF solution at room temperature, we demonstrated high fidelity replication of the 3D porous structures to biocompatible poly(glycidyl methacrylate) (PGMA) and elastomeric PDMS. We note that the whole fabrication process (template fabrication, infiltration and removal) was carried out at room temperature. Finally, we illustrated one potential application of 3D PDMS film as a reversibly color-changing, flexible photonic crystal.

5.2 Experimental methods

5.2.1 Fabrication of 3D POSS structures

The 3D POSS structure was fabricated by four-beam interference lithography following the procedure reported previously$^{20}$ using a visible diode-pumped Nd:YVO$_4$ laser ($\lambda=532$nm). The photoresist solution (~ 80 wt%) was formulated by mixing epoxycyclohexyl POSS® cage mixture (EP0408, Hybrid plastics) and 1.0 wt % Irgacure 261 (Ciba Specialty Chemicals) as visible photoinitiator in propylene glycol monomethyl
ether acetate (PGMEA, Aldrich). The film (thickness ~8 µm) was obtained by spin coating the photoresist solution on an O₂ plasma (PDC-001, Harrick Scientific Products, Inc.) cleaned glass at 2000 rpm for 30s. Since the glass transition temperature of the epoxy POSS precursor is rather low, ~ 3 °C by DSC (at a heating rate of 10°C/min), the film was prebaked at 50 °C for about 40 min and 95 °C for 2 min, respectively, to remove the solvent. After exposure to four-interfering beams (power of beam source ~ 0.7 w) for ~1s, the film was post-exposure baked at 50 °C for about 30 s and developed in PGMEA to remove unexposed or weakly exposed films, resulting in 3D microporous structures. To prevent the pattern collapse of the 3D film due to the capillary force upon drying in air, we dried the film using supercritical CO₂ dryer (SAMDRI®-PVT-3D, tousimis) after the pattern development.

5.2.2 Post-treatment of 3D POSS structures

The fabricated 3D POSS films were post-treated by O₂ plasma etching, and calcination in both O₂ and Ar environment, respectively. The O₂ plasma etching was performed in an O₂ plasma cleaner (PDC-001, Harrick Scientific Products, Inc.) at different time to achieve various filling volume fractions. The typical working power and pressure was 30 mW and 100 mTorr, respectively. In the calcination experiments, the samples were heated in a tube furnace purged with different gases at 500 °C and soaked for 1 hour at a heating rate of 3-10 °C/min. To test the ultrahigh temperature stability, we transfer the sample to Si substrate and placed the film in TGA chamber (TA instruments SDT 2960 simultaneous DTA-TGA) and heated to 1100 °C for 1hr in Ar.
5.2.3 Templating 3D PDMS and PGMA structures

For 3D PDMS, the PDMS prepolymer and curing agent (Sylgard 184 from Dow Corning) were mixed in a weight ratio of 10:1 and degassed for 2 hrs to remove air bubbles. The prepolymer mixture was then poured onto the POSS template at room temperature and waited for ~15 min to completely infiltrate the 3D porous template by capillary interaction. The composite film was cured at 65 °C for 2 hours, followed by HF aq. etching (~10 wt%) for ~50 min to remove the POSS template, resulting in an inverse 3D PDMS structure. During HF etching, a few droplets of dimethyl sulfoxide (DMSO) were added into the dilute HF solution (~10mL) to enhance the wettability on PDMS surface.

To prepare 3D PGMA, glycidyl methacrylate (GMA) monomers (Aldrich) were first mixed with 3 wt% of UV initiator (Darocur 1173, Ciba Specialty Chemicals) and prepolymerized by exposure to UV (97435 Oriel Flood Exposure Source) with a dosage ~1.0 J/cm². This viscous solution was then filled into the porous POSS template and covered by a transparent PDMS mold on top to reduce the exposure to O₂ in the air, which could inhibit the polymerization. This sandwiched sample was then exposed to UV light again with a total dosage of ~ 14.4 mJ/cm² followed by HF etching to remove the POSS template. No organic solvent was added in HF solution during etching.

5.2.4 Characterization.

The high resolution SEM images were taken from FEI Strata DB235 Focused Ion Beam (FIB) system at 5 kV. The lattice parameter in (111) plane was measured from the
top-view SEM images by average over 2 samples at three different locations by drawing lines in three different directions. The distance between the adjacent lattice planes in the [111] direction is measured from the focus-ion-beam milled cross-section. The samples were cut by FIB normal to the surface at an acceleration current of 1000 pA. The film shrinkage was estimated by comparing the measured lattice constants from SEM with the theoretically calculated values. Detailed calculation and reconstruction of the theoretical 3D structures were reported earlier.\textsuperscript{30} The Fourier Transform Infrared (FT-IR) spectra were acquired using Nicolet 8700 equipped with Nicolet Continuum Infrared Microscope. The samples were measured at a reflection mode with a MCT detector, and the aperture size used was about 80μm X 80μm. Energy-dispersive X-ray (EDX) analysis was performed on the 3D structures treated under different conditions using a high resolution field emission scanning electron microscope (FESEM) JEOL 7500F coupled to an Oxford Si/Li detector and INCA software to study the overall chemical compositions of the 3D porous structures. The EDX spectra were acquired and collected at an acceleration voltage 13 keV after optimizing the experiment conditions. The refractive index of the POSS film was determined by an AutoEL-II Null Ellipsometer (Rudolph Research, Flanders NJ) at a fixed incident angle, 70°, with a Helium-Neon laser source (\(\lambda = 632.8\) nm).

5.2.5 Optical photographs

The photographs of 3D POSS and PDMS structures were taken by digital camera (NIKON, D300). The two pictures from 3D POSS before and after sintering were taken
from two different samples at an illumination angle of ~45°. Both samples were from the same batch of 3D POSS fabricated under identical conditions. For the PDMS stretching experiments, the digital camera was located normal to the (111) plane of the 3D structure. The 3D PDMS film was clamped on two separated arms mounted on a custom-made ball bearing linear stage. The stretching strain was precisely controlled by the attached micrometer. Each frame was taken after the film was stretched to the desired strain level and hold for ~30 s.

Figure 5.1 Schematic illustration of epoxycyclohexyl functionalized POSS cage structure and its conversion to silica-like structures under different conditions.

5.3 Results and discussions

The 3D POSS structures were fabricated by four-beam interference lithography of the negative-tone resist, epoxycyclohexyl POSS (Figure 5.1).\textsuperscript{20} Compared to SU-8 materials, where 2 wt% photoacid generators (PAG) were used, 1% wt or less PAG was sufficient for the POSS photoresist, and the exposure time was half of that for SU-8 under the same exposure power. This can be attributed to the lower glass transition temperature
($T_g$) of epoxy POSS (~ 3ºC by differential scanning calorimetry, DSC) than that of SU-8 (50ºC). Therefore, the acid diffusion was much faster in epoxy POSS, resulting in a lower insolubility threshold. The resulting 3D structures were characterized by scanning electron microscopy (SEM). It is known that negative-tone photoresists have relatively large film shrinkage during photocrosslinking and developing steps when films become more densified.\textsuperscript{30, 31} Quantification of the shrinkage of the fabricated 3D POSS structures will be important to estimate the residual strain imposed in the film for later processing, and to predict the influence to the structural, mechanical and optical properties. First, we reconstructed the 3D structures based on SEM images obtained at different crystal planes (Figure 5.2), and compared the lattice constants to the calculated values. The detailed calculation and reconstruction of the theoretical 3D structures were reported earlier.\textsuperscript{30} A refractive index of 1.52 was used for epoxy POSS in our calculation, which was determined by ellipsometry measurement. As seen in Table 5.1, there is 48% shrinkage in the [111] direction but no shrinkage in the (111) plane, leaving large residual strain within the POSS film. The difference in shrinkage in different directions can be explained by the substrate confinement effect, where the porous structure can shrink freely in the vertical direction but is restricted in the horizontal plane.\textsuperscript{30, 32} The slightly larger shrinkage of 3D POSS in the [111] direction in comparison to SU–8 (41%)\textsuperscript{30} may be due to the lower molecular weight of the epoxy POSS precursor (with lower $T_g$), resulting in larger density change after photocrosslinking.
Table 5.1 Characteristics of diamond-like POSS structure fabricated by holographic lithography

<table>
<thead>
<tr>
<th>Materials</th>
<th>Pitch in the (111) plane</th>
<th>Distance between the adjacent lattice planes in the [111] direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental (µm)</td>
<td>0.98</td>
<td>0.68</td>
</tr>
<tr>
<td>Calculated* (µm)</td>
<td>0.98</td>
<td>1.30</td>
</tr>
<tr>
<td>Shrinkage (%)</td>
<td>0</td>
<td>48</td>
</tr>
<tr>
<td>Volume Shrinkage (%)</td>
<td></td>
<td>48</td>
</tr>
</tbody>
</table>

* obtained from level surface by considering the influence of refraction at the photoresist film/air interface.

Figure 5.2 SEM images of 3D POSS. a) Large view. b) Top view. c) Cross-sectional view. The sample was focus-ion milled and tilted at 45°.

Previously, we have studied the thermal and mechanical stability of the 3D epoxy POSS when sintered at 500°C in air to remove the organic contents (Figure 5.3). The 3D structure was found thermally stable up to 500°C in air or O₂, and the POSS film was converted to silica. However, micro-cracks appeared throughout the film (Figure 5.3) due to large mass loss and mismatch of coefficient of thermal expansion (CTE) between the porous silica structure and the glass substrate. While crack-free area could be found in
local domains (~ 100 x100 μm²), the formation of micro-cracks over mm² area remains undesirable for templating high index materials, which often requires high deposition temperature (400-800°C). In turn, it will decrease the quality of the film for potential photonic device application.

![Figure 5.3](image)

**Figure 5.3** SEM images of 3D POSS structures after calcination at 500 °C for 1 hour in O₂. (a) Large view. (b) Close-up view.

Orilall *et al.* recently have shown that heating the polystyrene colloidal templates under an inert atmosphere up to 900 °C converts the polymer into sturdy amorphous/graphitic-like carbon, which prevent the collapse of the macroporous structures.²⁸ To investigate whether this mechanism was applicable to our system, we performed thermal treatment under Ar atmosphere at a temperature varied from 500 °C to 1100 °C for 1hr. We found that the whole film was crack-free at 500°C in Ar in contrast to that heated in O₂ (see Figure 5.4), whereas cracks appeared at 1100°C, probably due to large thermal coefficient mismatch between the film and the substrate. Here, the film was transferred from a cover glass to a Si wafer since glass became softened above
1000°C. Compared to the original POSS structure, the pore size became bigger after calcination (Figure 5.4c) due to the large mass loss. Further, the optical photograph of the 3D POSS structure after thermal treatment in Ar (Figure 5.5b) appeared darker compared to that of as-fabricated one (Figure 5a), which might be due to the formation of carbon in the film. Surprisingly, no major microcracks were observed under optical microscope, which was further manifested by SEM images under different magnifications (Figure 5.4).

Figure 5.4 SEM images of 3D POSS structures after calcination at 500 °C for 1 hour under an Ar environment at different magnifications: a) 150 X b) 500 X and c) 50K X.
**Figure 5.5** Optical images of 3D POSS films a) before and b) after heating at 500 °C for 1 hour in Ar. The images were taken at the same light illumination angle of 45°.

In addition to the film quality, the filling volume fraction of the template, thus, the porosity of the inverse photonic crystal, plays an important role to open a complete bandgap. Thus, we attempted a second approach, i.e. a dry etching method using O₂ plasma, to remove the organic moieties at room temperature (Figure 5.2). Compare to thermal treatment, the latter approach will offer the flexibility to control the filling volume fraction. As seen in Figure 5.6, when the film was exposed to a low power (30W) O₂ plasma for 1 hr, a crack-free film over ~ 5 mm in diameter was obtained, whereas the skeleton of the 3D structure apparently became thinner (strut width, ~130 nm) (Figure 5.6b) in comparison to that of the original POSS film (~283 nm) (Figure 5.2b). If the film was remained in the plasma chamber continuously for a few hours, it became rather hot and micro-cracks were observed as those seen in the samples calcined in O₂ (see Figure 5.3). If the sample was taken out of the plasma chamber intermittently for cooling, then etched again, for example, for another 2hr and 40 min., the film remained crack-free, while the porosity was increased to 70% and the skeleton was as thin as ~78 nm (Figure 5.7a-b). When the total plasma time was increased to 5 hrs 40 min., the top surface of the porous structure began to collapse (Figure 5.7c), and the 3D structure was completely destroyed after O₂ plasma treatment for a total of 10 hrs (Figure 5.7d). Since the plasma etching is a top-down process, we have been curious about how uniform the etching was throughout the film. Surprisingly, in contrast to the result shown
in Figure 5.7c with long etching time, at a relatively shorter etching time (< 4hrs) the porosity and skeleton thickness were rather uniform throughout the film in the 3D structures according to the cross-sectional SEM images (Figure 5.6c and 5.7b). We think both the low etching intensity in our plasma chamber and relatively thin film of 3D structures (< 10 μm thick) may contribute to the rather uniform etching results. Nevertheless, the experiments demonstrated that we could vary the film porosity up to 80% before the 3D structure collapsed simply by changing the O₂ plasma treatment time, which would allow us to manipulate the photonic bandgap properties.

Figure 5.6 SEM images of 3D POSS structures after O₂ plasma etching (power of 30 W) for 1 hr. (a) Large view. (b) Top view. Inset: close-up view. (d) cross-sectional view.
Figure 5.7 SEM images of 3D POSS structures after O$_2$ plasma etching at different time: a-b) 3 hrs 40 min, c) 5 hrs 40 min, and d) 10 hrs in total. The films were continuously etched for 1-2 hrs before taken out and cooled down, and put back to chamber for etching. Scale bar: 1 μm.
To understand the underlying mechanism of the high fidelity 3D structures obtained after either thermal treatment in Ar or O₂ plasma, we investigated the chemical nature of the films in different processes using FT-IR and EDX spectroscopy analysis. As seen in Figure 5.8, we have identified ten IR bands: A (3000–3700 cm⁻¹), B (2800 –3000 cm⁻¹), C (1636 cm⁻¹), D (1350–1450 cm⁻¹), E (1245 cm⁻¹), F (1000-1150 cm⁻¹), G (1076 cm⁻¹), H (955 cm⁻¹), I (870-890 cm⁻¹), J (780-800 cm⁻¹). Some of the Si-O peaks and C-O ether or epoxy ring peaks overlap. The detailed assignment of the observed IR peaks is summarized in Table 5.2.

![FT-IR spectra of 3D POSS structures treated under different conditions.](image)

**Figure 5.8** FT-IR spectra of 3D POSS structures treated under different conditions.
Table 5.2 The observed IR peaks and their assignments for epoxy POSS films treated under different conditions.

<table>
<thead>
<tr>
<th>Peak</th>
<th>POSS after crosslinking</th>
<th>POSS after O₂ plasma</th>
<th>POSS 500°C in O₂</th>
<th>POSS 500°C in Ar</th>
<th>SiO₂*</th>
<th>Peak assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3000-3700</td>
<td>3000-3700</td>
<td>3000-3700</td>
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<td>-OH stretch</td>
</tr>
<tr>
<td>B</td>
<td>2800-3000</td>
<td>2800-3000</td>
<td>2800-3000</td>
<td></td>
<td></td>
<td>-CH₂ stretch</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td>1636</td>
<td></td>
<td>-C=O stretch</td>
</tr>
<tr>
<td>D</td>
<td>1350-1450</td>
<td>1350-1450</td>
<td></td>
<td></td>
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<td>-CH₂ deformation</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>1245</td>
<td>1272</td>
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<tr>
<td>F</td>
<td>1150-1000</td>
<td>1150-1000</td>
<td>1150-1000</td>
<td>1150-1000</td>
<td></td>
<td>-C-O-C ether stretch</td>
</tr>
<tr>
<td>G</td>
<td>1076</td>
<td>1076</td>
<td>1076</td>
<td>1087</td>
<td></td>
<td>-O-Si-O- short chain vibration</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>955</td>
<td></td>
<td></td>
<td></td>
<td>-Si-OH stretch</td>
</tr>
<tr>
<td>I</td>
<td>878</td>
<td>878</td>
<td>887</td>
<td></td>
<td></td>
<td>epoxy ring C-O-C deformation</td>
</tr>
<tr>
<td>J, J’</td>
<td>800</td>
<td>790</td>
<td>800</td>
<td>780</td>
<td>810</td>
<td>Si-C stretch</td>
</tr>
</tbody>
</table>

*: from ref 33

In comparison to the IR spectrum of SiO₂ as a reference, it is clear that all films contain a certain amount of carbon. Heating the film in O₂ removed most carbon, as evidenced with the disappearance of C-H stretch peak (B, 2970 cm⁻¹), and the film possessed a large quantity of Si-OH (see peaks A and H). The appearance of carbonyl peak C is probably due to the oxidation of the film. For the films heated at 500°C in Ar, a large amount of CH₂ groups (see peaks B and D) was removed but no -OH groups were formed in contrast to the film treated in O₂. The intensity of shoulder G (O-Si-O long chain) increased from the original POSS to O₂ plasma treated one, and became a rather
broad peak in film treated in Ar, indicating that the cage structures with O-Si-O short chains may have been collapsed into ladder or random structures.\textsuperscript{33,34} The appearance of E and shift of J (800 cm\textsuperscript{-1}) to J' (780 cm\textsuperscript{-1}) with increased intensity, both from Si-C stretch, further confirms the presence of carbon in the film treated in Ar.\textsuperscript{35} The POSS film after O\textsubscript{2} plasma treatment for 1 hr was nearly identical to that of the original film.

To quantify the elemental composition of the 3D POSS films treated under different conditions, we performed EDX mapping analysis. The film was transferred to an Al substrate before EDX mapping to eliminate substrate contribution of Si or O. As seen in Table 5.3, for a POSS film treated in Ar at 500\textdegree{}C for 1 hr, the O/Si ratio was close to 2. However, there was a significant amount of residual carbon, 28.83 wt\%, remained in the film, in contrast to a trace amount of carbon (1.67 wt\%) in the POSS film heated in O\textsubscript{2}. For the latter, the O/Si ratio was also close to 2, indicating nearly complete conversion of POSS to silica. For O\textsubscript{2} plasma treated (30 W, 1 hr) film, the C/Si ratio was nearly identical as the original POSS film, in agreement with FT-IR results, with 56.31 wt\% carbon remained in the film. Based on stoichiometric calculation, the residual carbon from the heat treatment in Ar should exist as amorphous/graphitic-like material as suggested by Orilall \textit{et al.}\textsuperscript{28} not silicon oxycarbide. Supporting this, the above treated templates could be easily removed by HF aq. solution (see discussion in the next section), whereas the silicon oxycarbide film is known not soluble in HF aq. solution.\textsuperscript{36} In any case, both FT-IR and EDX analysis suggested that the presence of carbon materials in the films enhanced the crack-resistance of 3D POSS structures.
Table 5.3 Elemental analysis of 3D POSS structures treated under different conditions.

<table>
<thead>
<tr>
<th>Element</th>
<th>Bare POSS film*</th>
<th>O₂ plasma treated</th>
<th>500°C in O₂</th>
<th>500°C in Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Relative weight (%)</td>
<td>Relative weight (%)</td>
<td>Relative atomic (%)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>58.54</td>
<td>56.31</td>
<td>66.88</td>
<td>1.67</td>
</tr>
<tr>
<td>O</td>
<td>24.39</td>
<td>28.47</td>
<td>25.39</td>
<td>56.68</td>
</tr>
<tr>
<td>Si</td>
<td>17.07</td>
<td>15.22</td>
<td>7.73</td>
<td>41.64</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

*: the composition was calculated based on chemical formulation of epoxy POSS provided by Hybrid Plastics, (C₈H₁₃O)ₙ(SiO₁.₅)ₙ

Since both the POSS film and its derivatives can be readily dissolved in HF aq. solution, they are attractive as robust and versatile templates for replication of a wide range of materials that can be processed either at low (e.g. organics, polymers) or high temperatures (e.g. semiconductors). The application of 3D POSS templates for fabrication of high index semiconductor photonic crystals will be discussed elsewhere. Here, we demonstrated the utility of 3D POSS structures for room-temperature templating of functional 3D polymeric structures, including PGMA and PDMS. Both of them are biocompatible, and their 3D porous structures are of interest as scaffold for tissue engineering. Moreover, PDMS is elastomeric. Its low Young’s modulus (1-3 MPa) makes it easily deformed under an external force or by exposure to an organic solvent. Recently such deformation has been harnessed for tunable phononic crystals.
Because epoxy POSS is highly transparent in the UV-vis region, we have successfully fabricated 3D POSS structures with film thickness up to 30 μm in comparison to < 5 μm using AZ5214. The inverse 3D PGMA and PDMS structures were obtained by first filling the viscous precursors into the porous POSS template, followed by photopolymerization (for PGMA) or thermal curing (for PDMS), and HF etching (Figure 5.11). Since PDMS is more hydrophobic than the POSS template, in order to remove the POSS template a little bit of organic solvent was added in the HF solution to achieve good wettability at POSS/PDMS interface. This solvent must be soluble in water, but should neither dissolve nor swell the PDMS film. Among many organic solvents, DMSO offers the ideal combination as the wetting solvent, which has a PDMS swelling ratio of 1.00. In our experiments, no apparent swelling was observed after the PDMS sample was immersed in DMSO for approximately two hours. In the case of PGMA replication, the HF aqueous solution has good wettabiliy on PGMA, thus, no organic solvent was added. To estimate the POSS etching time, a control experiment was first conducted by immersing a bare 3D POSS film in the same HF solution, which was found completely dissolved in less than 10 min. For the PGMA or PDMS/POSS composites, ~50 min was necessary to remove the POSS template.
As seen in Figure 5.10, the PGMA and PDMS precursors were completely filled into the templates and faithfully replicate the 3D diamond-like structures. Because the whole fabrication process was achieved at room temperature, including fabrication of template, infiltration of precursors and polymerization, and removal of the template, high fidelity films that were completely crack-free over entire sample area (~ 5 mm in diameter) were obtained. Compared to many reported templating processes using highly crosslinked negative-tone resist (e.g. SU-8), which requires high decomposition temperature (≥ 400°C in air) to remove the template, the POSS 3D structure is clearly advantageous and versatile for both high and low temperature templating. The fabrication procedure we demonstrated here can be straightforwardly applicable to many other materials, organic, hybrid, and ceramic materials, for fabrication of a wide range of 3D structures.
Finally, we illustrate the application of 3D PDMS film for flexible photonic switching. Since PDMS film is deformable in organic solvent\textsuperscript{40} and/or under mechanical stretching,\textsuperscript{41} 3D PDMS structures have been of interest as tunable photonic paper and inks\textsuperscript{42} and phononic crystals.\textsuperscript{5} Compared to solvent swelling-induced deformation, the use of mechanical force allows us to independently control the amount, direction (uniaxial or biaxial in planar directions or in vertical direction), and timing of strain applied to the PDMS film. This added controllability offers us flexibility to maneuver the porosity and lattice constant of the 3D structure, thus, optical properties \textit{in real time}. As seen in Figure 5.11, when the photonic film was stretched uniaxially in-plane, the hue of crystal color gradually changed from bright yellow, to red to dark green when the applied strain was increased from 0% to 22.6% (Figure 5.11b1-b8). When the strain was released, the color was completely recovered (Figure 5.11c1-c7, movie also available in Support Information). The wavelength of the structure color, $\lambda$, can be expressed by Bragg’s
equation with Snell’s Law: \( \lambda = 2d \sqrt{n_e^2 - \sin^2 \theta} \), where \( d \) is the interplanar spacing of the planes, \( n_e \) is the effective refractive index, and \( \theta \) is the angle of incident light. When stretched in (111) plane, lattice constants increased along the stretching direction while that decreased in the perpendicular direction due to Poisson’s ratio of PDMS (\( v=0.5 \)). These lattice-constant changes shift the optical path of the diffraction light accordingly, which in turn caused change of the diffraction color. Moreover, this color tuning of the PDMS sheet is reversible and repeatable. Detailed characterization of the stretched films and their manipulation will be reported elsewhere.

**Figure 5.11** Reversibly in-plane stretching 3D PDMS structures. (a) Schematics of stretching. (b-c) Optical images of 3D PDMS after reversibly stretching (b) and releasing (c) the strain at different levels. The color changed gradually as the strain was increased or decreased. b1,c7) 0%, b2,c6) 3.2%, b3,c5) 6.5%, b4,c4) 9.7%, b5,c3) 12.9%, b6,c2) 16.1%, b7,c1) 19.4%, and b8) 22.6%.
5.4 Conclusions

We fabricated diamond-like POSS structures through four-beam interference lithography, and studied their thermal and mechanical stability either under thermal treatment or by O$_2$ plasma. The 3D structure was maintained when calcined at a temperature up to 1100°C, and crack-free samples over a large area (~ 5 mm in diameter) were obtained when the POSS films were treated with a low intensity oxygen plasma or heated at 500°C under an Ar environment, in contrast to crack formation when thermally treated in O$_2$. FT-IR and EDX spectra analysis suggested there was a large quantity of residual carbon left in the crack-free samples to enhance the crack-resistance of the 3D structures. Further, we could fine-tune the filling volume fraction of the POSS 3D structures by varying the O$_2$ plasma treatment time and power. Since POSS and its derivatives could be easily removed by HF aq. solution at room temperature, we demonstrated the utility of the 3D POSS structures as templates for high fidelity replication of the 3D porous structures into functional polymers, including PGMA and PDMS. Notably, the whole process (template fabrication, infiltration and removal) was achieved at room temperature. Finally, we illustrated the application of 3D PDMS film as a reversible and repeatable color-changing, flexible photonic crystal. We believe that the organosilicate structure demonstrated here offers a thermally and mechanically robust yet versatile template for replication of a wide range of materials at both low and ultrahigh processing temperatures. The presented high fidelity templating and tuning of the optical
properties of the replicated 3D PDMS films will provide important insights to create novel materials that are potentially useful for a wide variety of technological applications.

5.5 References


Chapter 6
3D non-oxide ceramic photonic crystals for ultrahigh temperature applications

In Chapter 5, 3D POSS structure has been converted to thermally stable silica-like structure, and it is removable by HF solution at room temperature. We have successfully templated 3D photonic crystals to biocompatible poly(glycidyl methacrylate) (PGMA) and elastomeric poly(dimethylsiloxane) (PDMS) without any thermal treatment. Here, we investigate the fabrication of 3D non-oxide ceramic photonic crystals using 3D POSS structure as highly robust template that are processed at an ultrahigh temperature, 1100 °C.

6.1 Introduction

Photonic crystals that are thermally and mechanically robust are of immense interests for various applications, including thermal barrier coatings (TBC), energy conversion to electricity, thermophotovoltaics (TPV), and thermoelectric.\(^1\) Specifically, in order to increase the efficiency of gas turbines, a thermal barrier coating has to be applied in the combustor chamber where the typical temperature is above 1000 °C.\(^2,3\) Metallic photonic structures have been fabricated for ultrahigh temperature applications,\(^4-7\) however, they are very subjective to degradation and early failure by corrosive products formed by impurities, such as nitroxide, sulfur, chlorine and water.\(^8\) Therefore,
translucent ceramics are often used as TBCs to provide thermal protection for metallic components upon exposure to high-temperature environments.

Oxide barrier coatings have shown high resistance to water vapor corrosion at high temperature, but they often have relatively low toughness.\(^9\) In comparison, non-oxide ceramics, such as silicon carbide (SiC)\(^{10-12}\) and boron carbide (BC),\(^{13, 14}\) have superior hardness, high melting points, low densities, and excellent thermal stability. Specifically, SiC has high refractive index, thus, photonic crystals made from SiC could potentially offer wide photonic band gaps that provide barrier properties in omni directions with high efficiency.\(^{15-17}\) Therefore, it has emerged as a promising material in TBC applications,\(^1\) and those require high performance under extremely harsh conditions.\(^{18}\)

While many groups have demonstrated 1D photonic crystals as thermal barrier coatings,\(^{19-22}\) none has attempted 3D ceramic photonic crystals for ultrahigh temperature applications. To fabricate a photonic crystal with large and complete photonic bandgaps, it often requires backfilling of high index inorganic materials into a 3D template. Recently different chemistry and templating strategies have been developed to create 3D PCs with high refractive index contrast.\(^{22-26}\) However, most of these templates will decompose at a temperature above 500 °C,\(^{27}\) therefore, are not compatible with the ultrahigh processing temperature (typically > 1000 °C), which is required to convert the perceramic precursors to non-oxide ceramics.

Previously, we have demonstrated crack-free 3D hybrid microstructures when treating the 3D epoxy functionalized POSS at 500 °C under Ar or by oxygen plasma.\(^{28}\)
Compared to conventional polymeric materials, which decompose completely above 500 °C,\textsuperscript{27} the hybrid POSS is thermally and mechanically robust. In addition, the 3D POSS structures could be readily removed by HF solution at room temperature, we have successfully replicated the 3D photonic crystals to biocompatible poly(glycidyl methacrylate) (PGMA) and elastomeric poly(dimethylsiloxane) (PDMS) without any thermal treatment. Here, we demonstrated the fabrication of 3D non-oxide ceramic photonic crystals from SiC and BC by infiltrating SiC precursor, allyl-hydrido-poly-carbo-silane (AHPCS), and BC precursor, bis(decaboranyl)hexane (BDH) (Figure 6.1), respectively, through capillary action, followed by pyrolysis at 1100 °C under an argon environment (Figure 6.2a and 2b). The inverse 3D ceramic photonic crystals were obtained after the removal of template by HF aq. solution (Figure 2c). 3D SiC and BC photonic crystals were found thermally stable above 1100 °C under Ar. The optical properties of 3D PCs were characterized at different stages, and found matching well with the calculated values determined by MIT Photonic Bandgap (MPB) calculations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{chemical_structures.png}
\caption{Chemical structures of the template material, POSS and backfilled ceramic precursors.}
\end{figure}
Figure 6.2 Schematic illustration of the fabrication of 3D ceramic photonic crystals templated from 3D POSS structures.

6.2 Experimental methods

6.2.1 Fabrication of 3D POSS structures

The 3D POSS structure was fabricated by four-beam interference lithography following the procedure reported earlier\textsuperscript{27} using a visible diode-pumped Nd:YVO4 laser ($\lambda = 532$ nm). The photoresist solution (~ 80 wt\%) was formulated by mixing epoxycyclohexyl POSS® cage mixture (EP0408, Hybrid plastics) and 1.0 wt % Irgacure 261 (Ciba Specialty Chemicals) as visible photoinitiators in propylene glycol monomethyl ether acetate (PGMEA, Aldrich). The POSS film (thickness ~8 µm) was obtained by spin coating the photoresist solution on an oxygen plasma (PDC-001, Harrick Scientific Products, Inc.) cleaned silicon wafer at 2000 rpm for 30s. The film was prebaked at 50 °C for ~40 min and 95 °C for 2 min, respectively, to remove the solvent. After exposure to four-interfering beams (power of beam source ~ 0.7 w) for ~1s, the film was post-exposure baked at 50 °C for 30 s and developed in PGMEA to remove
unexposed or weakly exposed films, resulting in 3D microporous structures. 3D films were dried in a supercritical CO₂ dryer (SAMDRI®-PVT-3D, tousimis) to prevent pattern collapse.

**6.2.2 Templating 3D non-oxide ceramic photonic crystals**

For 3D SiC photonic crystals, the AHPCS liquid precursor (from Starfire Systems, Inc. and used as received) was infiltrated into 3D POSS template (~ 8 µm thick) by capillary force. In order to avoid the formation of an overlayer on top of the template, we placed a droplet of AHPCS at the edge of the 3D POSS structure, and kept for ~ 30 min. to allow for complete infiltration of AHPCS. The infiltrated sample was then converted to ceramics at 1100 °C for 1 hr at a heating rate of 10 °C/min in a thermal gravimetric analysis (TGA) sample pan (TA instruments, SDT 2960 simultaneous DTA-TGA) purged with argon. After cooling down to room temperature naturally, the sample was immersed in an HF aq. solution (~20 wt%) for ~ 4 hrs to remove the POSS template, followed by rinse with DI water for at least 5 times. The bulk silicon carbide film was also prepared by spin coating AHPCS onto a silicon wafer with a thickness > 8 µm, followed by pyrolysis under the same condition as that for 3D SiC.

For pyrolysis experiments under vacuum, the 3D POSS and AHPCS bulk films were supported on Si wafers, and heated to both 1100 °C and 1300 °C, at a heating rate 10 °C/min, and held for 1 hr. The chamber pressure was maintained at ~1 x 10⁻¹⁵ mTorr.

3D BC was obtained by melting the BDH precursor at 140 °C into the pre-heated POSS template (~3 µm thick) in a similar fashion as that of SiC, where the filled sample
was kept on the hot plate for 10-20 min. before pyrolysis at 1100 °C for 1 hr in the TGA sample pan under Ar. BDH was synthesized according to the procedure reported earlier.29

6.2.3 Characterization

High resolution SEM images were taken from FEI Strata DB235 Focused Ion Beam (FIB) system at 5 kV. The lattice constant in the (111) plane was measured from the top-view SEM images by average over 2 samples at three different locations, each drawing lines in three different directions. The distance between the adjacent lattice planes in the [111] direction was measured from the FIB milled cross-section. The samples were cut by FIB normal to the surface at an acceleration current of 1000 pA. The film shrinkage was estimated by comparing the measured lattice constants to the theoretically calculated values.30 The FT-IR spectra were acquired from Nicolet 8700 equipped with Nicolet Continuum Infrared Microscope. The samples were measured at the reflection mode with a MCT detector in [111] direction, and the aperture size was about 80 μm x 80 μm. The photonic bandgap properties of the crystal structures obtained at different processing steps were calculated by MIT Photonic-Band Package, where the refractive indices of 1.52,28 1.4531 and 2.6531 were used for POSS, silica and silicon carbide respectively. Energy-dispersive X-ray (EDX) analysis was performed on a high resolution field emission scanning electron microscope (FESEM) JEOL 7500F coupled to an Oxford Si/Li detector and INCA software to study the overall chemical compositions and
distribution of the chemical elements in the 3D structures. The EDX spectra were collected at an acceleration voltage of 13 KeV. Since the 3D SiC films were thick (~8 µm), samples were supported on a silicon wafer for EDX measurement after confirming the same element compositions on a tantalum substrate. For 3D BC since the film was thin (~3 µm), it was transferred to a tantalum substrate for EDX to eliminate the substrate contribution to element compositions.

6.3 Results and discussions

The silicon carbide precursor, AHPCS, is a yellowish viscous liquid at room temperature, which can be infiltrated directly into the 3D porous template by capillary force. As seen from the cross-sectional view SEM image of the POSS template filled with AHPCS, followed by pyrolysis at 1100 °C in Ar for one hour (Figure 6.3a), the template was nearly completely filled with SiC. The small gap between the template and infiltrated SiC from top-view SEM image (Figure 6.3a inset) could be attributed to the large mismatch of thermal coefficient of expansion between POSS (or silica) and SiC at 1100 °C. After HF etching, the inverse 3D SiC structure was obtained (see Figure 6.3b).
Figure 6.3 SEM images of (a) Template/SiC pyrolyzed at 1100 °C in Ar and (b) inverse 3D SiC after HF etching to remove the template. Insets: top view SEM images at a higher magnification, scale bar: 500 nm.

Boron carbide precursor, BDH, is a powder at room temperature, therefore, it was melted at ~140 °C to facilitate the infiltration into the POSS template by capillary force. As seen from Figure 6.4b, an inverse 3D BC crystal was also obtained after the template removal, similar to the results from 3D SiC crystals. The slightly closed top surface (insets in Figure 6.4a and 4b) was due to the over-infiltration of the template.
Figure 6.4 SEM images of (a) template/BC pyrolyzed at 1100 °C in Ar and (b) inverse 3D BC structure after HF etching to remove the template. Insets: top view SEM images at a higher magnification, scale bar: 500 nm.

To confirm the ceramic formation within 3D structures, we investigated the corresponding elemental compositions using energy-dispersive X-ray (EDX) mapping analysis, and compared the data to that of bulk ceramic films treated under the same condition. As seen in Table 6.1, both silicon carbide and boron carbide were formed after pyrolysis and template removal. Under Ar gas, however, the stoichiometry ratio of Si: C is ~ 1:3.46 mol/mol in 3D structures and ~ 1:1.29 mol/mol in bulk film, and a large amount of residual oxygen is always present in both 3D structures and the bulk films. Compare to the oxygen content in the silicon carbide bulk film obtained at 1100 °C under an Ar environment, 9.17%, the 3D silicon carbide structure had much more residual oxygen, 17.63 %. We think this may be attributed to the oxidation reactions caused by the trace amount of O₂ in the Ar gas, and the 3D porous structure has much larger surface area than the bulk film. Supporting this, the 3D POSS structure was nearly completely
converted into silica with only 2.37% residual carbon after pyrolysis under the same heat treatment condition. Likewise, there is a small amount of oxygen, 5.37%, in 3D BC (B:C ~ 1.64 mol/mol), although it is somewhat less than that in 3D SiC.

To reduce the residual oxygen content caused by the oxidation reactions, we performed pyrolysis under vacuum. As seen from Table 6.1, compared to the film treated at 1100 °C in Ar, the bulk SiC film obtained at 1100 °C under vacuum has slightly less oxygen, 7.55% vs. 9.17%. Correspondingly, the oxygen content in 3D POSS was reduced from 68.74% (under Ar) to 47.86% (under vacuum), and the carbon enriched silica-like material was formed. Based on stoichiometric calculation, the residual carbon should exist as amorphous/graphitic-like material as suggested by Orilall et al.32 Our recent work has shown that the presence of carbon materials in the films enhanced the crack-resistance of 3D POSS structures.28 Since the above treated template could be readily removed by HF aq. solution, the carbon in the film should be amorphous rather than in the form of silicon oxycarbide, which is not soluble in HF aq. solution.33,34

In order to further reduce the residual oxygen, we increased the pyrolysis temperature to 1300 °C under vacuum, and oxygen-free bulk SiC film was obtained vs. 7.55% at 1100 °C. Interestingly, we found that 3D POSS structure was also successfully converted into SiC with oxygen free. Compared to the templating method, only one processing step is involved in the conversion from 3D POSS to SiC.
Table 6.1 EDX analysis of POSS, silicon carbide and boron carbide films pyrolyzed at 1100 °C or 1300 °C for 1hr under an Ar or vacuum environment. Except the 3D BC film, all films were supported on Si substrates.

<table>
<thead>
<tr>
<th>Materials</th>
<th>C Weight %</th>
<th>C Atomic %</th>
<th>O Weight %</th>
<th>O Atomic %</th>
<th>Si (for silicon carbide) or B (for boron carbide) Weight %</th>
<th>Si (for silicon carbide) or B (for boron carbide) Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D POSS, under Ar&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.47</td>
<td>2.37</td>
<td>56.70</td>
<td>68.74</td>
<td>41.83</td>
<td>28.89</td>
</tr>
<tr>
<td>3D POSS, under vacuum&lt;sup&gt;a&lt;/sup&gt;</td>
<td>19.74</td>
<td>28.99</td>
<td>43.40</td>
<td>47.86</td>
<td>36.86</td>
<td>23.15</td>
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<tr>
<td>3D POSS, under vacuum&lt;sup&gt;b&lt;/sup&gt;</td>
<td>34.97</td>
<td>55.70</td>
<td>0</td>
<td>0</td>
<td>65.03</td>
<td>44.30</td>
</tr>
<tr>
<td>3D SiC, under Ar&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>63.59</td>
<td>17.97</td>
<td>17.63</td>
<td>32.85</td>
<td>18.36</td>
</tr>
<tr>
<td>Bulk SiC film, under Ar&lt;sup&gt;a&lt;/sup&gt;</td>
<td>32.78</td>
<td>51.17</td>
<td>7.83</td>
<td>9.17</td>
<td>59.39</td>
<td>39.65</td>
</tr>
<tr>
<td>Bulk SiC film, under vacuum&lt;sup&gt;a&lt;/sup&gt;</td>
<td>29.98</td>
<td>48.40</td>
<td>6.23</td>
<td>7.55</td>
<td>63.79</td>
<td>44.05</td>
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<tr>
<td>Bulk SiC film, under vacuum&lt;sup&gt;b&lt;/sup&gt;</td>
<td>33.12</td>
<td>53.66</td>
<td>0</td>
<td>0</td>
<td>66.88</td>
<td>46.34</td>
</tr>
<tr>
<td>3D BC, under Ar&lt;sup&gt;a&lt;/sup&gt;,&lt;sup&gt;c&lt;/sup&gt;</td>
<td>38.23</td>
<td>36.44</td>
<td>5.37</td>
<td>3.84</td>
<td>56.40</td>
<td>59.72</td>
</tr>
</tbody>
</table>

<sup>a</sup>Samples were treated at 1100 °C for 1 hr.
<sup>b</sup>Samples were treated at 1300 °C for 1 hr.
<sup>c</sup>Supported on a tantalum substrate.

At the mean time, we studied the lattice constants of 3D structures obtained from different stages (Table 6.2). The lattice parameter in (111) plane was measured from the
top-view SEM images by average over two samples at three different locations. At each location, we drew lines in three different directions. The distance between the adjacent lattice planes in the [111] direction was measured from the focus-ion-beam (FIB) milled cross-section with the FIB normal to the sample surface. Compared to the 3D POSS structure, the SiC filled composite (Figure 6.5) has about 13.2% shrinkage in the vertical direction and 19.4% shrinkage in the (111) plane. The relatively larger shrinkage in the (111) plane and thermal coefficient of expansion mismatch between the film and the substrate (Si) led to many microcracks in the pyrolyzed sample. Locally, there were single domain crack-free over at least 100 μm by 100 μm, which we used SEM for characterization. After removal of the template by HF etching, we can see that there is almost no change in the lattice constants of the inverse 3D SiC structure (see Table 6.2).

**Table 6.2** Comparison of lattice constants of 3D POSS and silicon carbide structures obtained at different stages*.

<table>
<thead>
<tr>
<th></th>
<th>3D POSS</th>
<th>3D template/SiC pyrolyzed at 1100 °C in Ar</th>
<th>Inverse 3D SiC after HF etching</th>
<th>Inverse 3D SiC with additional sintering at 1100 °C in vacuum</th>
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<td>Distance between the adjacent planes in the [111] direction (μm)</td>
<td>0.68</td>
<td>0.59</td>
<td>0.59</td>
<td>0.57</td>
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</tbody>
</table>

*: all films were supported on Si substrates

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Figure 6.5 SEM image of POSS filled with SiC after pyrolysis at 1100 °C under an Ar environment. The film was FIB milled in perpendicularly to the (111) plane with an output current of 1000 pA and sample tilt at 45°.
Figure 6.6 SEM images of inverse 3D SiC seen in Figure 6.5 with additional pyrolysis at 1100 °C for 1hr under vacuum. a) Top view. b, c) Cross-sectional views in different plane directions. d) Cross-sectional view of the sample FIB milled in perpendicularly to the (111) plane with an output current of 1000 pA, and sample tilt at 52°.

To further test the thermal stability of thus obtained inverted 3D ceramic photonic crystals for ultrahigh temperature applications, we reheated the inverse 3D SiC crystal at 1100 °C under vacuum for one hour. As seen in Figure 6.6 the 3D structure is well-maintained, indicating high thermal stability. Further, only a small shrinkage, 3.8% and 3.3% in the (111) plane and [111] direction, respectively (Table 6.2) was observed.
compared the 3D SiC crystal before and after the additional sintering at 1100 °C under vacuum.

**Figure 6.7** FTIR reflectance spectra of 3D diamond-like structures in the [111] direction. a) 3D POSS template. b) 3D template/SiC, pyrolyzed at 1100 °C in Ar. c) Inverse 3D SiC. In each panel, the left figure is a simulated spectrum and the right one is the experimental FTIR spectrum.

To further evaluate the corresponding photonic bandgap properties of these new materials, we used FT-IR to quantitatively measure the reflectance of the 3D photonic crystals, including the POSS template, backfilled SiC/template composite, and the inversed SiC, obtained at different processing steps and compare them with the calculated PBG. As seen in Figure 6.7 a stop band peak at 1.78 μm was observed for pure POSS. In the SiC/template composite, there is a bathochromic shift of the reflection peak to ~2.45 μm. This is probably due to the increase of mean refractive index of SiC/template structure. However, a blue shift, 1.84 μm, was observed for the inverse SiC 3D structure

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after removal of the template since the mean refractive index is decreased. Further, we note that the peak reflectivity increased significantly from 0.8 (3D POSS) to 2.0 (inverse 3D silicon carbide photonic crystal), indicating increased optical quality of the films.

We also noticed that the SiC/template sample was much more colorful and its reflectivity (6.2) was higher than that of the inverse SiC (2.0). This result is different from our previous results from titania infiltrated polymer template. This may be attributed to the air gap between the SiC and the template structure (Scheme 2e). At the mean time, the mean refractive index for SiC/template is higher than that of inverse 3D SiC. Overall, the high mean refractive index and high refractive index contrast contribute to the high reflectivity. The experimental reflectivity peak positions at different processing stages agree with the calculated bandgaps, further supporting the quality of the backfilling and the resulting 3D non-ceramic photonic crystals. In calculation, we considered the reflective index of POSS, template, and SiC where the refractive indices of 1.52, 1.45 and 2.65 respectively. In the SiC/template structure we considered ~5% air and 52.5% SiC filling volume fraction during the PBG calculation and.

**6.4 Conclusions**

We have demonstrated fabrication of 3D photonic crystals from non-oxide ceramics, including silicon carbide and boron carbide, by using 3D POSS structures as templates. The inverse 3D porous silicon carbide structure was stable up to 1100 °C under vacuum condition. The measurement of film reflectivity in the [111] direction before and after the
ceramic conversion in comparison to the calculated photonic bandgap properties suggested that 1) the template was nearly completely filled by the pre-ceramic precursors, and 2) the photonic structure was well-preserved after the removal of the template.

6.5 Reference


Chapter 7

Summary and Outlook

7.1 Summary

The goal of this thesis is to fabricate 3D photonic crystals with complete bandgaps. We used holographic lithography to pattern diamond-like structures from various photoresists, followed by infiltration of the polymer templates with high refractive index inorganic and polymeric materials. Along the lines, we investigated different types of photoresists, including negative tone and hybrid resist, and their shrinkage, and thermal and mechanical stability during 3D fabrication, infiltration and template removal. For backfilling, we studied different backfilling strategies, including electrodeposition, capillary infiltration, melting and chemical reduction, to create high index photonic crystals from TiO$_2$, Si and non-oxide ceramics (SiC and BC), respectively, as well as functional polymers (e.g. PGMA and PDMS).

The polymer photonic crystals fabricated by MBIL technique do not have a complete bandgap due to the low refractive index, therefore, they are always used as templates for infiltration of inorganic materials with high refractive index, followed by removal of the template. Although a variety of photonic crystals have been fabricated from various templating approaches, it remains challenging to obtain high fidelity photonic crystals over a large area for practical applications due to 1) the large shrinkage of the photoresist film, 2) low thermal stability of the polymer template, 3) incomplete filling, and 4) difficulty of removal of the template while maintaining the film crack-free.
To address above problems, we investigated each processing step during fabrication of 3D photonic crystals, from polymer template fabrication, backfilling to template removal. In each step, we compared the experimental results to simulation to elucidate the mechanisms. Along the line, we studied 1) the photoresist chemistry to minimize the shrinkage, from volume shrinkage of 42% from conventional SU-8 to 5.9% from narrowly dispersed PGMA, 2) backfilling strategies for complete infiltration, including electrodeposition, capillary force, and melting, 3) fabrication of 3D template from epoxy functionalized POSS, which can be removed at room temperature by HF etching, O₂ plasma etching and thermal decomposition under Ar atomosphere to minimize crack-formation, and 4) the application of POSS template for both low and ultrahigh temperature process to fabricate 3D polymeric and non-oxide ceramic PCs, respectively.

In Chapter 2, we demonstrate the fabrication of diamond-like SU-8 structures using MBIL. From SEM top views and the FIB milled cross-sectional view, we measure the lattice constants of diamond-like structures and quantify the film shrinkage by comparing the experimental data with the calculated values after considering the refractive effect at the air-film interface. We find ~41% shrinkage in the vertical direction normal to the (111) plane, however, only 1% shrinkage in the (111) plane that is parallel to the substrate surface.

In order to reduce the shrinkage, in Chapter 3, we have designed and synthesized a new negative-tone photoresist, PGMA, with different molecular weights with narrow distribution. We find that 3D PGMA structures have a lower shrinkage in [111] direction, 18%, than structures fabricated from SU8 under the same conditions (41%), which may
offer better control of the photonic bandgap properties of PCs templated from this material.

The study of the backfilling of holographically patterned polymer templates through sequential silica/silicon CVD and ALD process finds it challenging to completely fill the triply periodic bicontinuous templates. In the top-down infiltration processes, core-shell morphology is often revealed as the deposited materials grow conformally and continuously on the 3D template surface to fill the interstitial pores. Because the pore sizes are not uniform throughout the bicontinuous template, the surface of pore network tends to pinch off (i.e., disconnects) at the narrowest pore channels before the interstitial voids are completely filled, resulting in loss of photonic bandgap properties.

In order to get away from the pinch-off problem, in Chapter 4, we backfill the holographically patterned diamond-like SU-8 templates with titania sol-gel using the electrodeposition technique. A bottom-up filling mechanism is suggested, resulting in nearly complete backfilling of titania. We find that the electrodeposition proceeded in two stages: at the early stage of electrodeposition (< 60 min), a thin titania conformal coating formed on the surface of polymer template, creating a seed layer that is critical for further electrodeposition; in the second stage the deposition occurred preferentially from the film bottom layer end up with bottom-up mechanism. SEM images suggest that the template is completely filled.

After calcination at 500 °C, the polymer template is removed, leading to inversed 3D titania photonic crystal. Our studies show that a combination of pre-annealing step and a slow heating rate was important to form a dense 3D anatase titania crystal without pattern collapse. The optical properties of the 3D photonic crystals are measured at various
processing steps, which matches well with the simulated photonic bandgaps (PBGs) and the SEM observation, further confirming that the polymer template is nearly completely filled with titania by the bottom-up process.

Since the polymer template is highly cross-linked, it cannot be removed simply by dissolution process. Calcination above 400°C in air, however, creates a lot of microcracks and defects that are not applicable for practical devices. In Chapter 5, we design and fabricate 3D hybrid microstructures from photosensitive organosilicates, epoxy functionalized POSS, as versatile photonic templates. The POSS structure can be readily removed by HF etching, making it suitable for room temperature processing without generating cracks during the infiltration and template removal steps. At the mean time, we convert the 3D POSS structures into crack-free silica-like templates with high fidelity over the entire sample area (~5 mm in diameter) by either thermal treatment in Ar at 500°C or O₂ plasma, and the porosity can be conveniently controlled by O₂ plasma power and time. The converted silica-like structures are found thermally and mechanically stable and the 3D structure is maintained when calcined at a temperature up to 1100°C. Our studies show that a large quantity of residual carbon left in the crack-free samples, thus, enhancing the crack-resistance of the 3D structures.

Because the POSS and its derivatives could easily dissolve in HF aq. solution at room temperature, it allows us to template functional and high temperature sensitive organic polymers, including PGMA and poly(dimethyl siloxane) (PDMS). All the fabrication processes are conducted at room temperature, including template fabrication, infiltration and removal. Further, we illustrate the application of 3D PDMS film as a reversible and repeatable color-changing, flexible photonic crystal.
The silica-like templates converted from POSS structures are thermally and mechanically stable. In Chapter 6, we demonstrate fabrication of 3D non-oxide ceramic structures, which are sintered at 1100 °C, including SiC and BC, using 3D POSS structures as templates. Typically at such a high temperature, conventional polymer structures will decompose and collapse. The inverse 3D ceramic photonic crystals are obtained after HF etching, which are found stable up to 1100 °C under vacuum condition. The measured optical properties of the 3D structures at different processing stages match very well with the simulation.

7.2 Outlook

The study presented in this thesis offers critical insights for mass production of high fidelity and high refractive index photonic devices over a large area, as well as applications, such as microfluidics, microporous cell-culture scaffolds and sensors.

For the 3D PDMS structures, here we only demonstrate color tuning by changing the unidirectional mechanical strain. However, the field is still wide open for tunable 3D porous structures. Understanding the relationship between the geometry response and the external force will help us design and engineer complex structures and new materials. For instance, we and others have demonstrated the pattern transformation of 2D elastomeric membranes by solvent swelling-induced instability and mechanical compression,\(^1\),\(^2\) which may have applications in photonics, surface plasmonics, phononics and negative Poisson ratio materials.\(^3\) However, the pattern transformation in 3D structures has not been studied. With 3D POSS structures as templates, we can
fabricate thick films (up to 30 µm) from 3D PDMS structures, which are not accessible by other techniques.

Because the 3D POSS structures are thermally and mechanically robust even at ultrahigh temperatures, they offer new opportunities to create thermal barriers using non-oxide ceramic photonic crystals at ultrahigh temperatures. Our recent results from X-ray Diffraction (XRD) suggest that the 3D porous POSS structure could be directly converted into 3D SiC structure at 1300 °C under vacuum condition. However, all the 3D SiC crystals are converted to 3D oxide above 1100°C in air. To further increase the thermal stability /oxidation resistance, it will be necessary to study backfilling of different types of non-oxide ceramic materials, for example, doping SiC.

Another potential direction is to couple the complete infiltration by electrodeposition with the easily removable POSS templates to deposit electrolyte materials, which are not soluble in acid aq. solution, for example, creating 3D metamaterials for the interest of negative-index materials, and light emitting devices.

**7.3 References**


Appendix A

Positive tone photoresist, PHOST-co-PtBMA

Figure A.1 Schematic illustration of a) synthesis of positive tone resist of PHOST-co-PtBMA, and b) the chemistry in photolithography.
Figure A.2 SEM image of 2D holes fabricated from PHOST-co-PtBMA through three beam interference lithography. The inset shows the tilt view at 45°.
Compare to the AZ5214 photoresist (Table 1.1), \( t \)-butyl group based positive tone resist has many advantages, such as easy to get a thick film and transparent in visible light. In addition, it has been found exceptionally thermal stable, even at the temperatures above the \( T_g \) of the material, 150 °C.\(^1\) Therefore it has been named as an environmentally stable chemical amplification positive (ESCAP) resist,\(^2,3\) which could be a good candidate for a polymer template. This resist resin can be synthesized through radical polymerization of \( t \)-butyl methacrylate (tBMA) with 4-acetoxy styrene (AOS) in toluene initiated by 2,2’-azo-bis(isobutyronitrile) (AIBN), followed by selective base hydrolysis with ammonium hydroxide in methanol (see Scheme A1.1a)\(^1\). Typically the monomer molar ratio (Hydrotoxystyrene/\( t \)-Butyl Methacrylate) is about 9:1 in the random copolymer PHOS-\( co \)-PrBMA. After exposure, the PAG releases the acid catalyst, which will decompose the \( t \)-butyl group into isobutene through a chemical amplification reaction process during the PEB process (Scheme A1.1b). In the high light density area, the tBMA is converted into methacrylate acid (MA), which is soluble in aqueous base. In the unexposed or weakly exposed area, the resist will remain forming a positive-tone pattern.\(^4\) Figure A1.1 shows the SEM images of 2D holes fabricated from positive tone resist PHOS-\( co \)-PrBMA by using MBIL technique with a three-beam set up, the inset shows the 2D sample at a tilt view of 45°. From Figure A1.1, it can also be seen that the positive-tone photoresist gives a high resolution and a very high contrast with sharp vertical walls in the holes. More importantly, the positive tone resist PHOS-\( co \)-PrBMA is soluble in methanol, so it can be easily removed when used as template.
References


Appendix B

3D Si/C composite templated from organosilicate structure by holography lithography

B.1 Experimental methods

B.1.1 Fabrication of 3D POSS structures

The 3D POSS structure was fabricated by four-beam interference lithography following the procedure reported previously¹ using a visible diode-pumped Nd:YVO4 laser (λ=532nm). The photoresist solution (~ 80 wt%) was formulated by mixing epoxycyclohexyl POSS® cage mixture (EP0408, Hybrid plastics) and 1.0 wt % Irgacure 261 (Ciba Specialty Chemicals) as visible photoinitiators in propylene glycol monomethyl ether acetate (PGMEA, Aldrich). The POSS film (thickness ~8 µm) was obtained by spin coating the photoresist solution on an oxygen plasma (PDC-001, Harrick Scientific Products, Inc.) cleaned silicon wafer at 2000 rpm for 30s. Since the glass transition temperature of the epoxy POSS precursor is rather low, ~ -3 °C by DSC (at a heating rate of 10°C/min), the film was prebaked at 50 °C for ~40 min and 95 °C for ~2 min, respectively, to remove the solvent. After exposure to four-interfering beams (power of beam source ~ 0.7 w) for ~1s, the film was post-exposure baked at 50 °C for ~30 s and developed in PGMEA to remove unexposed or weakly exposed films, resulting in 3D microporous structures. To prevent the pattern collapse of the 3D film due to the capillary force by air drying, we dried the film using supercritical CO₂ dryer (SAMDR®-PVT-3D, tousimis) after the development.
B.1.2 Conversion of 3D POSS template into 3D Si/C composite structure

The silicon wafer supported POSS template and magnesium granules were placed at opposite ends of a steel ampoule that was then welded shut. Such ampoules were thrust into a tube furnace that had been preheated to 650 °C, and then held at this temperature for 6 h (at 650 °C, the oxygen partial pressure is only $1.7 \times 10^{-57}$ atm). The reaction process was determined by the color change of the reacted samples, which means, the conversion was assumed complete when there was no further color change observed on the film. The sample was then immersed in a 1M HCl solution (molar HCl:H$_2$O:EtOH ratio = 0.66:4.72:8.88) for 4 hr at room temperature to selectively dissolve the magnesia. An HF solution (molar HF:H$_2$O:EtOH ratio = 1.05:1.11:6.45) was used to etch any silica formed during the exposure to the aqueous HCl solution. Both the HCl and HF treatment were conducted in glove box purged with ultrahigh-purity argon gas. The oxygen partial pressure in the glove box was maintained below 0.1 ppm. After that, the sample was then shipped from Georgia Institute of Technology to University of Pennsylvania for characterization.

B.1.3 Characterizations

B.1.3.1 Scanning Electron Microscope

The high resolution SEM images were taken from FEI Strata DB235 Focused Ion Beam (FIB) system at 5 kV. The lattice parameter in (111) plane was measured from the top-view SEM images by average over 2 samples at three different locations by drawing lines in three different directions. The distance between the adjacent lattice planes in the [111] direction is measured from the focus-ion-beam milled cross-section. The samples
were cut by FIB normal to the surface at an acceleration current of 1000 pA. The film shrinkage was estimated by comparing the measured lattice constants from SEM with the theoretically calculated values. Detailed calculation and reconstruction of the theoretical 3D structures were reported earlier.²

**B.1.3.2 Fourier Transform Infrared**

The Fourier Transform Infrared (FT-IR) spectra were acquired using Nicolet 8700 equipped with Nicolet Continuum Infrared Microscope. The samples were measured at a reflection mode with a MCT detector in [111] direction, and the aperture size used was about 80μm X 80μm. The photonic bandgap properties of the crystal structures obtained at different processing steps were calculated by MIT Photonic-Band Package,³ where the refractive indices of 1.52 (determined by an AutoEL-II Null Ellipsometer, Rudolph Research, Flanders NJ, at a fixed incident angle, 70°, with a Helium-Neon laser source, λ = 632.8 nm), 1.45,⁴ 2.38,⁴ 3.45⁴ and 1.74⁴ were used for POSS, silica, carbon, silicon and MgO respectively. The sample was exposed to the air during the FTIR measurement which will probably cause oxidation of the converted silicon material into silica.

**B.1.3.3 Energy-dispersive X-ray**

Energy-dispersive X-ray (EDX) analysis was performed on a high resolution field emission scanning electron microscope (FESEM) JEOL 7500F coupled to an Oxford Si/Li detector and INCA software to study the overall chemical compositions and the distribution of the chemical elements of interest in the 3D porous structures. The EDX spectra were acquired and collected at an acceleration voltage 12 keV after optimizing the experiment conditions. The Si/C composite samples were supported on silicon wafer
substrate for EDX measurement after a control experiment on aluminium substrate confirming the samples were thick (~8 µm) enough without substrate contribution.

B.1.3.4 Optical photography

The photographs of 3D POSS and Si/C composite structures were taken by digital camera (NIKON, D300), which was located normal to the (111) plane of the 3D structure. The two pictures from 3D POSS before and after chemical conversion were taken from two different samples at an illumination angle of ~45°. Both samples were from the same batch of 3D POSS fabricated under identical conditions.

B.2 Results

Table B.2.1 The observed IR peaks and their assignments for POSS template, 3D Si/C composite structure before and after etching

<table>
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<th>Peak</th>
<th>POSS template</th>
<th>3D Si/C composite before etching</th>
<th>3D Si/C composite after etching</th>
<th>SiO₂*</th>
<th>Peak assignment</th>
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<tr>
<td>A</td>
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<td>3065-3660</td>
<td>3267-3750</td>
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<tr>
<td>B</td>
<td>2815-3021</td>
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<td>-</td>
<td>-CH₂ stretch</td>
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<tr>
<td>C</td>
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<td>1425-1521</td>
<td>1400-1500</td>
<td>-</td>
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<tr>
<td>D</td>
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<td>1152</td>
<td>1152</td>
<td>1186</td>
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<td>1087</td>
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<tr>
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<td>800</td>
<td>810</td>
<td>Si-C stretch</td>
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*: from ref⁵
Table B.2.2 EDX analysis for 3D Si/C composite structures obtained at different stages

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<th>Si</th>
<th>Mg</th>
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<td></td>
<td>Weigh %</td>
<td>Atomi c %</td>
<td>Weig ht %</td>
<td>Atomi c %</td>
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<td>3D silicon before HCl and HF etching</td>
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<td>3D structures</td>
<td>Silicon substrate supported 3D POSS</td>
<td>Converted 3D silicon before HCl and HF etching</td>
<td>Converted 3D silicon after HCl and HF etching</td>
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Figure B.2.1 SEM image of a) 3D POSS template and b) 3D Si/C composite structure before HCl and HF etching
Figure B.2.2 SEM image of the 3D Si/C composite structure after HCl and HF etching in different views: a) large view, b) top view, c) blow up view and d) FIB drilled cross section and tilt at 45°
Figure B.2.3 FT-IR spectra of 3D structures under different stages
Figure B.2.4 Optical images of 3D POSS films supported on silicon wafer substrate a) before and b) after the magnesiothermic reduction process. The images were taken at the same light illumination angle of $45^\circ$. 
Figure B.2.5 FTIR reflectance spectra of 3D diamond-like structures in the [111] direction for: a) POSS template, 3D Si/C composite structure b) before and c) after HCl etching to remove the magnesia followed by HF etching to remove the residual silica. In each panel, the left figure is a simulated spectrum and the right one is the experimental data.
B.3 Reference


Appendix C

List of publications


