Fabrication of 3-D photonic band gap material of TiO2 by microtransfer molding and sol-gel processing

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Fabrication of 3-D photonic band gap material of TiO$_2$ by microtransfer molding and sol-gel processing

by

Jijun Huang

A thesis submitted to the graduate faculty in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE

Major: Materials Science and Engineering

Major Professor: Dr. K. P. Constant

Iowa State University
Ames, Iowa
2000
This is to certify that the Master's thesis of

Jijun Huang

has met the thesis requirements of Iowa State University

Signatures have been redacted for privacy
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ABSTRACT

Photonic band gap (PBG) crystals are artificially engineered periodic dielectric structures which exhibit frequency regions in which electromagnetic (EM) waves cannot propagate in certain directions. By using the "master mold" with desired features, an elastomeric mold of poly (dimethylsiloxane) (PDMS) with a relief structure on its surface was shaped. From these elastomeric molds, one-, two-, and multi-layer PBG samples were formed using microtransfer molding. The sol-gel solutions with the precursor of titanium diisopropoxide bis (2, 4-pentadionate)(TDBP), tetraethyl orthotitanate (TEOT) and titanium isopropoxide (TIPP) were infiltrated into the samples, respectively by spin coating. The infiltrated samples were sintered at 550 °C. The sintered samples were characterized by optical microscopy, SEM and FTIR.

Results show that the sintered samples experience large shrinkage (up to 40%) during heat treatment and therefore the structures had a low filling ratio. The filling ratio can be enhanced by increasing the concentration of the precursor in the sol-gel. FTIR data showed that there were strong absorption peaks around 1500 cm⁻¹ with a transmittance of 92.5% due to the existence of the first band gap of PBG structures. A sintered 4-layer sample was successfully obtained by infiltrating the sol of TDBP (26wt%) six times into the pattern through spin coating. It is likely that this approach can yield high quality three-dimensional PBG structures of TiO₂.
CHAPTER 1: INTRODUCTION

Photonic band gap (PBG) crystals are artificially engineered periodic dielectric structures which exhibit frequency ranges in which electromagnetic (EM) waves cannot propagate in certain directions. The behavior of electromagnetic waves in such modulated dielectric structures can be viewed as analogous to the behavior of electrons propagating in a periodic lattice potential in crystals. The Bragg-like diffraction from periodic arrangements of atoms or molecules in semiconductors opens up forbidden energy band gaps. Similarly, in photonic band gap crystals, the destructive interference of multiple scattering events at the dielectric interfaces (or scattering centers) gives rise to frequency gaps in photon energy bands. Since the concept of photonic band gap crystals was first proposed by Yablonovitch in 1987 ¹, these structures have received considerable attention theoretically and experimentally ², ³, due to their potential uses over a broad frequency range, extending from microwave to optical regimes.

Photonic band gap crystals have many unique features. Band gaps can exist only in the directions of dielectric periodicity because scattering occurs along that direction. For a complete 3D frequency gap, electromagnetic modes are totally suppressed inside the gap region, regardless of the polarization. The structures then behave like ideal reflectors in all the directions. Similar to impurity doping of semiconductor crystals, localized EM modes (evanescent modes) can be created in the band gap region of PBG structures by disturbing the periodicity of the dielectric structures ⁴. By adding extra dielectric materials to PBG crystals, a donor-like defect is introduced near the higher band edge, while removing some of the material gives rise to a acceptor-like defect mode near lower band edge. Likewise, surface modes are generated by the termination of dielectric periodic structures as well.
Another important feature of PBG crystals is that their band gap characteristics are scalable to any length scales, ranging from microwaves to optical frequencies and beyond. Note that in semiconductor systems, the length scale is usually set by Bohr radius.

Photonic band gap materials have immense potential for creating a whole new class of optical devices which, if realized, could result in optical circuits and communications devices as powerful and versatile as electronic circuits. The fundamental advance that PBG materials offer is the ability to amplify, channel, and control the propagation of electromagnetic radiation in much the same way that semiconductor devices and metallic wires do for electricity. With PBG materials, for example, one can make resonant cavities for light amplification, suppress unwanted optical losses, and make light execute the sharp turns needed for circuit miniaturization.

By incorporating nonlinear optical and other advanced materials into PBG crystals, optical switches and so-called “smart materials” can be fabricated. It has been shown theoretically and experimentally (in the microwave region) that the face centered cubic (FCC) lattice is favored for photonic band gaps. To show a band gap in the optical region, the structure must have a lattice parameter between 0.4 and 1 µm and a refractive index difference of at least 2. As in electronic band gap devices (semiconductors), in photonic band gap materials, some of the most useful materials are those with well-controlled defect states.

There are several possible routes to fabricating PBGs. The use of conventional semiconductor device fabrication techniques has proven to be very difficult. A novel method for fabricating these materials is needed. A direct approach might be to use monosize titania spheres (dielectric constant ~2.5) to construct an FCC lattice. Although the processing of monosized powders has advanced significantly in recent years, highly uniform TiO$_2$ has not yet been synthesized and the variation in sphere size prohibits close packing. Also, calculations
indicate that the conjugate structure produces a more dramatic photonic gap. Therefore, the optimal structure would be that in which a high dielectric materials is located in the interstices of an FCC-packed array of "air" atoms. Recent advances in the area of using elastomeric stamps for the formation of patterned surfaces at the micron level suggest that this technology might be used to develop a novel approach for constructing these photonic band gap materials. This technique can be used to make a template from which a PBG crystal can be made. The next step is to fill this template with appropriate materials.

The sol-gel process has attracted increasing interest over the last decades because it permits the development of new materials and new shaping routes (fibers, thin films, and near net shape objects) with good homogeneity and good purity. Moreover, the sol-gel process is very effective for ceramic materials that must be sintered into a dense body. The very fine structure of the gel enables the sintering to be achieved at low temperatures compared with green bodies prepared by classic ceramic processing. Sol-gel processing, whereby a solution or sol densifies, consists of the following steps: solution or sol, gelation into a colloidal gel network, drying of a three-dimensional porous solid, sintering to a dense crystalline shape. Several additional steps may be involved in preparing the precursor or sol, especially in multicomponent systems. In any sol-gel process, the chemistry of the precursor materials is controlled to induce particle-particle interactions or polymer chain interactions that result in the encapsulation of the solvent(s) by the colloidal solid. Without the addition of a dispersed solid, the open networks typically undergo at least 50% linear shrinkage during solvent removal and thermal consolidation to form a dense shape.

The advantages of this process include control of the purity of the reagents, control of the degree of homogeneity of mixing of the precursors, potential control of the phase evolution and microstructure, and opportunity for fabrication into useful, non-traditional shapes such as
fibers, thin films, bubbles, optical elements, patterned surfaces etc. Due to the remarkable ability to tailor ceramic materials to exhibit specific properties, the increasing family of sol-gel applications now includes optical, electronic, and structural ceramics.

The goal of this work is to demonstrate the fabrication of 3-dimensional photonic band gap materials of TiO$_2$ by utilizing microtransfer molding and sol-gel processing. To construct a photonic band gap structure, a master mold with the desired features must be created from which a flexible polymer mold can be shaped. The design and fabrication of the master mold depends upon the desired optical properties. In this work, a low frequency (large dimension) mold was used for proof of concept. As a part of this work, an elastomeric mold with a relief structure was fabricated using the procedure developed for use in microcontact printing (µCP). In general, the elastomeric mold is made from poly (dimethylsiloxane) (PDMS). Using this elastomeric mold, one-layer, two-layer, three-layer and multi-layer samples were constructed on a slide glass or silicon substrate.

One of the main tasks of this work is to explore the infiltration of the sol-gel into the sample resulting from the microtransfer molding. The formation of sol-gel solutions from different precursors including titanium diisopropoxide bis (2, 4- pentadionate) (TDBP), tetraethyl orthotitanate (TEOT) and titanium isoproproxide (TIPP) was investigated. Other variables investigated include the pH value of the sol, the ratio of precursor to water, the ratio of alcohol to water, and synthesis procedures. At the same time, the effect of the infiltration of the solution on the desired pattern of the sample and infiltration techniques were also probed so that a good sample can be obtained. Another part of main tasks is to form the desired ceramic TiO$_2$ patterns by sintering the infiltrated samples. The sintering conditions were studied and optimized to produce the highest quality samples. The highest quality samples are expected to
have a uniform distribution of ceramic TiO$_2$, minimum cracking, minimum shrinkage and no deformation of the pattern of TiO$_2$.

A significant part of this work lies in the characterization of the samples. The scanning electron microscopy (SEM) was utilized to examine the morphology of the pattern, the alignment, the long-range order, and the distribution of the TiO$_2$ ceramics. The transmission and reflection optical spectra as a function of wavelength were used to obtain the presence, location, width and the depth of the photonic band gap.

In this thesis, Chapter 2 will present previous work on photonic band gap structures, microtransfer molding and microcontact printing, and sol-gel processing. The experimental procedure will be described in Chapter 3 with regard to the design and fabrication of one-, two- and multi-layer samples, formation of the sol-gel, infiltration of sol-gel into the sample, heat treatment and sintering and characterization of sintered samples. Chapter 4 presents and discusses the results of this study. In the end, conclusions are made in Chapter 5 and suggestions for future work are given in Chapter 6.
CHAPTER 2: LITERATURE REVIEW

This work contains elements of three distinct areas: photonic band gap materials, microtransfer molding and sol-gel processing. Relevant literature on these topics is reviewed in this chapter.

2.1 Photonic Band Gap Structure

The theory of a photonic band gap was first proposed by Yablonovitch in 1987. The idea is analogous to the behavior of electrons in a crystal lattice. The electromagnetic waves propagating in a structure with a periodically modulated dielectric constant are organized in "photonic bands" which are separated by "gaps" where propagating states are forbidden.

Following the inception of this idea, various lattice geometries were studied to find a periodic structure that would exhibit a photonic band gap in all directions. With these findings, Yablonovitch and Gmitter employed the concepts of band theory to describe the behavior of electromagnetic waves in three dimensionally periodic face-centered-cubic (FCC) dielectric structures, revealing that it was desirable for the Brillouin zone in reciprocal space to be as near to spherical as possible. The lowest-order Brillouin zone for the FCC structure happens to be nearer to spherical than the Brillouin zone of any other common crystal structure. It was found that most FCC dielectric structures have "semimetallic" band structure (near infrared), and that one particular dielectric "crystal" (Emerson & Cumming Stycast-12) which actually has a "photonic band gap" could be identified. This dielectric structure requires a refractive-index contrast greater than 3 to 1, which happens to be readily obtainable in semiconductor materials.

The existence of complete band gaps depends on lattice symmetry, direction of periodicity, ratio of the refractive indices between two materials in the structure, and filling
factor. It was first predicted by Ho, Chan, and Souloulis at Iowa State University that a 3D periodic crystal with diamond-like lattice symmetry would have a full band gap. It was found from theoretical calculations that these structures could show complete band gaps either with dielectric spheres placed at the diamond lattice sites or air spheres embedded in a high dielectric material as long as the diameters of the spheres were appropriately chosen and the refractive index contrast is greater than 2. This threshold can be explained with the fact that significant scattering effects occur only when the variation of dielectric constants is large enough. The photonic band gaps become wider as the ratio of refractive indices increases.

Moreover, the size of band gap can be optimized with a gap/midgap ratio of ~0.3 (forbidden gap normalized to the midgap frequency) by choosing the diameter of the air spheres to be 0.65a, where a is the lattice constant. In this case, the air spheres overlap with each other to form connected regions for both air and dielectric materials. Midgap $\omega_g$ is defined by $\omega_g = \xi (1/\langle n \rangle) (c/a)$ where c is the speed of light, a is the cubic lattice constant (repeat distance) of the periodic structure, and $\langle n \rangle$ is the square root of the volume-averaged dielectric constant of the material. The proportionality constant $\xi$ is governed by the dielectric constant contrast ratio and the geometrical structure of the periodic material, and can be determined numerically from calculation. Therefore, this structure can be considered to have two interpenetrating diamond lattices. It also implies that photonic band gap crystals can be created by connecting the sites of diamond lattice by dielectric rods or tubes. Figure 1 shows the first Brillouin zone of the FCC structure and the calculated band structure for a diamond dielectric structure consisting of dielectric spheres of refractive index 3.6 in an air background. Figure 2 demonstrates the relationship between gap to midgap frequency ratio and filling ratio, and the relationship between gap to midgap frequency ratio and refractive index.
Figure 1 First Brillouin zone of the FCC and the calculated photonic band structure for a diamond dielectric structure consisting of dielectric spheres of refractive index 3.6 in an air background. The filling ratio of the dielectric material is 34%. The frequency is given in units of c/a, where a is the cubic lattice constant of the diamond lattice. Ho, Chan, Soukoulis, Physical Review Letter, 65, 3152-3155, 1990.

Yablonovitch et al. 12 fabricated the first three-dimensional photonic band gap structure: the face-centered-cubic case employing nonspherical atoms. The structure was arranged in a periodic face-centered-cubic lattice, but with cylindrical air holes, giving it an overall diamond lattice structure. The periodicity in the structure was achieved by drilling holes 120° apart and at 35° from the z-axis into a dielectric slab (Stycast) as shown in Figure
Figure 2 (a) Gap to midgap frequency ratio ($\Delta \omega / \omega_c$) as a function of filling ratio for the case of dielectric spheres in air and air spheres in dielectric. The refractive index of the material is chosen to be 3.6. (b) $(\Delta \omega / \omega_c)$ as a function of refractive index contrast for a fixed dielectric structure. The dotted line is for the case of air spheres in dielectric with a filling ratio of 81%, and the solid line is for dielectric spheres in air with a filling ratio of 34%. Ho, Chan, Soukoulis, Physical Review Letter, 65, pp. 3152-3155, 1990.

3. This experimental structure exhibited a full 3-D photonic band gap. It had a forbidden gap from 13 to 16 GHz with 10 dB attenuation per unit cell.

However, the structure has proven difficult to fabricate at optical frequencies where feature sizes are less than one micron. Chemically assisted ion beam etching technology has been used to etch the holes. It has been found difficult to be to maintain the linearity and hole size as the etching depth increases. This adversely affects the periodicity of the structure.
and hence the photonic band gap. The midgap optical reflectivity is found to be very sensitive to structural errors in the photonic crystal.

After the initial verification of the existence of photonic band gap, there was an increased effort to find new structures that could be easily fabricated. Another structure that exhibited a complete band gap was suggested by Ho et al.\textsuperscript{13} and fabricated by Ozbay et al.\textsuperscript{15} from Iowa State. This “layer-by-layer” structure was fabricated by stacking layers of equally spaced round or rectangular rods as shown in Figure 4. The first layer-by-layer structure was fabricated using alumina rods with dielectric constant $\varepsilon = 9.6$ (microwave region) glued together to form a face-centered-tetrahedral symmetry. This structure was found much easier to scale down in size\textsuperscript{16}. Standard silicon micromaching techniques have been used to scale down the size of layer-by-layer PBG structure and make it operational up to 500 GHz at Iowa State.

Experimental demonstration of complete photonic band gap in a graphite structure was made by Lourtioz et al.\textsuperscript{17}. These experiments were performed at microwave frequencies from 27 to 75 GHz using hexagonal lattices of alumina rods. Transmission spectra were found to be in excellent agreement with numerical calculations. Attenuations larger than 30 dB were measured for structures comprised of only four rows of alumina rods.

The preparation of photonic crystals made of air spheres in titania was explored by Wijnhoven and Vos\textsuperscript{18}. Three-dimensional crystals of air spheres in titania (TiO$_2$) with radii between 120 and 1000 nanometers were made by filling the voids in artificial opals by precipitation from a liquid-phase chemical reactions and subsequently removing the original opal material by calcination. These artificial opals were formed from monodisperse polystyrene (PS). These macroporous materials were a new class of photonic band gap crystals for the optical spectrum. Scanning electron microscopy, Raman spectroscopy, and optical
Figure 3 First three dimensional dielectric PBG structure fabricated by drilling holes at 35° to normal and 120° to each other. Yablonovitch et al, Physical Review Letters, 67, 2295-2298, 1991.

Figure 4 Layer-by-layer structure developed by Iowa State University's group. Ho, Chan, Soukoulis, Biswas, Sigalas, Solid State Comm., vol. 89, pp. 413-416, 1994.
microscopy confirmed the quality of the samples, and optical reflectivity demonstrated that the crystals contained the structure needed to exhibit band gap behavior.

A visible-near infrared range photonic crystal made up of Si nanopillars was explored by Poborchii et al.\textsuperscript{19}. A two-dimensional square lattice of Si nanopillars (SQLN) for prospective applications in waveguides was used. Si nanopillars with a radius of $r = 32\pm 5$ nm were fabricated on the (100) surface of crystalline Si using the self-formed etching mask method. Reflection spectra of SQLN with the period of 270 nm (lattice parameter) were studied for different surrounding media, namely air and water. SQLN was shown to display photonic band gap (PBG) behavior in the visible-infrared spectral range.

Subramania, Constant, Biswas\textsuperscript{20} et al. investigated the optical photonic crystals fabricated from colloidal systems of monodisperse polystyrene with the diameter ranging from 395 to 770 nm. Using ceramic technique involving the simultaneously ordering of the spheres and formation of titania network, photonic crystals of close-packed arrays of air spheres in a dielectric background of titania were fabricated. It was showed that the photonic crystals exhibited a reflectance peak and a uniform color at the position of the first stop band. It was also indicated that the wavelength of the reflectance peak scaled very well with the sphere size.

2.2 Microcontact Printing and Microtransfer Molding

Microcontact printing (µCP)\textsuperscript{21} is a new technique for forming patterns with micron dimensions. It offers experimental simplicity and flexibility in forming certain types of patterns. Microtransfer molding was developed from microcontact printing with considering the formation of 3D complex microstructures of organic polymers and ceramics.
A method involving patterning of a self-assembled monolayer (SAM) on a gold substrate were reported by Kumar and Whitesides \textsuperscript{22} in 1993 using an elastomer stamp which was fabricated either from a phenol-formaldehyde polymer or polydimethylsiloxane, followed by selective etching in an aqueous, basic solution of cyanide ion and dissolved dioxygen (1M KOH, 0.1 M KCN). The authors demonstrated that the fabrication of Au pattern using PDMS was possible using the following steps. First PDMS was used to fabricate a stamp from a master template. The stamp was removed from the master by peeling away the cured polymer. Then the stamp was exposed to the alkanethiol ink. After inking, the stamp was brought into contact with the Au substrate. Finally, the patterned substrate was then etched in an aqueous, basic solution of cyanide ion and dissolved oxygen to produce the desired features. Through this technique, several types of features having dimensions ranging from 1 µm to several hundred µm were fabricated.

Two- and three-dimensional crystallization of polymeric microspheres by micromolding in capillaries was probed by Kim, Xia and Whitesides \textsuperscript{23}. They described the fabrication of crystalline 2D and quasi 3D arrays of microspheres, patterned in the plane of the support, using a technique they referred to as MIMIC (micromolding in capillaries) that was developed for the fabrication of polymeric microstructures of organic materials. Using MIMIC, they were able to fabricate 2D and 3D arrays of polystyrene microspheres in enclosed, continuous channels formed by conformal contact between a support and an elastomeric master whose surface was patterned with relief regions.

Zhao, Xia and Whitesides \textsuperscript{24} examined the fabrication of three-dimensional microstructure using microtransfer molding in which a new technique, microtransfer molding (µTM) for forming complex, three-dimensional microstructures of organic polymers and ceramics was described. In this technique, structures were shaped by filling microchannels on
the surface of an elastomeric mold with a liquid precursor, and then bringing the mold into contact with a planar or contoured substrate. The liquid precursor solidified in situ either thermally or photochemically. The elastomeric mold is then peeled away, leaving the resulting microstructures on the surface of the substrate.

Figure 5a shows a schematic procedure used for µTM. An elastomeric mold (usually from poly (dimethylsiloxane)(PDMS) with a relief structure on its surface was fabricated using the procedures developed for use in microcontact printing (µCP). The thickness of the PDMS mold used here was controlled to be < 2 mm to ensure the flexibility of the mold. A drop of liquid prepolymer was placed on the patterned surface of the mold and the excess prepolymer was removed. The most common method of removing excess polymer was to scrape it away using a piece of flat PDMS; alternatively, with appropriate structures the excess polymer could be removed by blowing off the surface of the mold with a brisk stream of nitrogen. Sometimes, both methods were used. The filled mold was then placed in contact with a substrate.

The prepolymer was then fully cured thermally or photochemically and the mold was peeled away. Figure 5b outlines the process used to fabricate multilayer structures using µTM. The procedure involved putting some liquid epoxy into the mold then playing upside down onto the mold with a precured, filled relief structure and peeling away when fully curing occurred.

2.3 Sol-Gel Processing

A sol is a dispersion of solid particles in a liquid phase where the particles are small enough to remain suspended indefinitely by Brownian motion. For aqueous sols, this means a particle size less than approximately 1 µm.
Sols are classified as lyophobic if there is a relatively weak solvent/particle interaction and lyophilic if this interaction is relatively strong. A gel is a solid containing a liquid component and an internal network structure so that both the solid and the liquid are in a highly dispersed state. Not all sols can be converted to gels. Although sols are thermodynamically unstable, they can be made kinetically stable by the imposition of an energy barrier that the particles must overcome to form a bound state. The three origins of this energy barrier are the development of a surface charge, steric hindrance, and solvation.
Sol-gel chemistry is usually based on the hydrolysis and condensation of metal alkoxides. At the functional group level, the reaction are usually described as

**Hydrolysis:** \(-\text{M-OR} + \text{H}_2\text{O} \rightarrow \text{M-OH} + \text{ROH}\)

**Condensation:** \(-\text{M-OH} + \text{RO-M} \rightarrow \text{-M-O-M} + \text{ROH}\)

Condensed species are formed as these reactions proceed leading to oxopolymers and then hydrous oxide \(\text{MO}_n \times \text{H}_2\text{O}\) when an excess of water is added. Such a description of sol-gel chemistry is far too simple and does not explain why chemical additives have to be added in order to control the growth of inorganic oxopolymers.

Actually, most sol-gel reactions involve hydroxylated species and can be described as nucleophilic substitutions:

\[
\text{M} \,(\text{OR})_n + m \, \text{XOH} \rightarrow [\text{M(OR)}_{n-m}(\text{OX})_m] + m \, \text{ROH}
\]

Where \(\text{X}\) stands for \(\text{H}\) (hydrolysis), \(\text{M}\) (condensation) or \(\text{L}\) (complexation), \(\text{L}\) being an organic or inorganic ligand. These reactions can be described according to an \(S_N2\) mechanism,

\[
\begin{align*}
\text{X} & \quad \text{M}^{8+} - \text{O}^{5-} - \text{R} \\ & \quad \text{H}^{8+} - \text{O}^{5-} - \text{R} \\
& \quad \text{X} - \text{M} - \text{O}^{5-} - \text{R} \\
& \quad \text{XO} - \text{M} - \text{O}^{5-} - \text{R} \\
& \quad \text{XO} - \text{M} + \text{ROH}
\end{align*}
\]

(1) nucleophilic addition of a negatively charged \(\text{HO}^{5-}\) group onto the positively charged metal atom \(\text{M}^{8+}\). This first step leads to an increase of the coordination number of the metal atom in the transition state;

(2) transfer, within the transition state, of the positively charged proton toward one negatively charged OR group;
(3) departure of the positively charged protonated alkoxide ligand ROH.

As a result of these reactions, the OR group is replaced by an OX group. The chemical reactivity of metal alkoxides toward hydrolysis and condensation then depends on the positive charge of the metal atom, $\delta_M$, and its ability to increase its coordination number, N. As a general rule, the electronegativity of metal atoms decreases, their size increases and the chemical reactivity of the corresponding alkoxides increases when going down the periodic table (Table 1).


<table>
<thead>
<tr>
<th>Alkoxide</th>
<th>$E_N$</th>
<th>$\delta_M$</th>
<th>r(Å)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(OPr)$_4$</td>
<td>1.74</td>
<td>+0.32</td>
<td>0.40</td>
<td>4</td>
</tr>
<tr>
<td>Ti(OPr)$_4$</td>
<td>1.32</td>
<td>+0.60</td>
<td>0.64</td>
<td>6</td>
</tr>
<tr>
<td>Zr (OPr)$_4$</td>
<td>1.29</td>
<td>+0.64</td>
<td>0.87</td>
<td>7</td>
</tr>
<tr>
<td>Ce(OPr)$_4$</td>
<td>1.17</td>
<td>+0.75</td>
<td>1.02</td>
<td>8</td>
</tr>
</tbody>
</table>

Gelation occurs within several days after water is added. Hydrolysis and condensation rates have to be increased via acid or base catalysis. The hydrolysis rate of Ti(OEt)$_4$ ($k_h = 10^{-3}$ M$^{-1}$ S$^{-1}$) is about five orders of magnitude greater than that of Si(OEt)$_4$ ($k_h=5\times10^{-9}$ M$^{-1}$ S$^{-1}$) $^{27}$.

The sensitivity of metal alkoxides toward hydrolysis and condensation depends on the steric hindrance of the alkoxy groups. The sensitivity decreases when the size of the OR groups increases. The choice of the solvent is therefore very important for the sol-gel synthesis
of metal oxides. Even with a given precursor, different solvents can lead to different products. The specific surface area of silica gels prepared from Si(OMe)₄ and heated to 600 °C, for instance, increases from 170 m²/g to 300 m²/g and the mean pore diameter decreases from 36 Å to 29 Å when EtOH is used as a solvent instead of MeOH. This is due mainly to alcohol interchange reaction ³¹.

Hydrolysis and condensation rates also depend on the molecular structure of the metal alkoxides. In the case of titanium alkoxides, for example, monomeric precursors such as Ti(OPr)₄, in which Ti is only four-coordinate, react very quickly with water, leading to the uncontrolled precipitation of polydispersed TiO₂. The reaction is much slower with oligomeric precursors such as [Ti(OEt)₄]ₙ, in which Ti has a higher coordination number.

Ti(Obu)₄ ³² is currently preferred as a precursor to TiO₂. It does not react too fast with water and can be handled without too much care. This is because O-n-Bu, with four carbon atoms, is the largest alkoxy group that does not prevent oligomerization. It gives mainly trimeric species, [Ti (O-n-Bu)₄]₃, when dissolved in benzene and dimeric species, [Ti(O-n-Bu)₄, BuOH]₂, in its parent alcohol.

The formation of condensed species also depends on the hydrolysis ratio ³² h = H₂O/M:

1. Molecular clusters are formed when a very small amount of water is used (h<1). Condensation is then governed mainly by the formation of μ-OR and μ-oxo bridges. Molecular oxo-alkoxides such as Ti₅O₄(OEt)₂₀ (h=0.6), Ti₁₀O₈ (OEt)₂₄ (h=0.8), and even Ti₁₆O₁₆(OEt)₃₂ (h=1) have been obtained via the controlled hydrolysis of Ti(OEt)₄. These compounds have been characterized by x-ray diffraction and ¹⁷O NMR.

2. For very large hydrolysis ratios (h≈10), all alkoxy groups are removed and an oxide network is formed. Moreover, the high dielectric constant of the aqueous medium
leads to the acid or base dissociation of the surface OH groups, and the resulting 
oxide gels are very similar to those obtained from aqueous solutions.

3. Between these two extremes, alkoxy groups are not completely hydrolyzed. They 
remain bonded to the growing oxide network giving rise to oxopolymers. Such 
polymeric species are often very suitable precursors for the deposition of thin films. 
Good adhesion with oxide substrates is obtained via the condensation of the 
remaining OR ligands with the hydroxyl groups at the surface of the substrate. 
Organics are then removed upon calcination at around 300 °C and a transparent 
oxide thin film is finally obtained.

Another factor affecting the hydrolysis and condensation is catalyst. The effects of a 
variety of catalysts on the overall hydrolysis and condensation rates, as judged by the times 
required for gelation, have been summarized by Pope and Mackenzie\textsuperscript{33} for TEOS hydrolyzed 
with four equivalents of water in ethanol (r=4). Their results, listed in Table 2, show not only 
the effects of hydronium ion and hydroxyl ion on the gel times but also the effects of the 
conjugate case, most notably $\text{F}^-$. Most of the properties of HF catalyzed gels are similar to 
those of base-catalyzed gels, which suggests that the roles of $\text{OH}^-$ and $\text{F}^-$ are similar.

Because of coordination expansion, most metal alkoxides other than silicon are highly 
reactive toward hydrolysis and condensation. They must be handled in a dry atmosphere; 
otherwise, hydrolysis occurs. Therefore, their chemical reactivity has to be decreased to avoid 
uncontrolled precipitation. This can conveniently be performed via the chemical modification 
(or complexation) of the molecular precursor.

Metal alkoxides react with hydroxylated compounds XOH such as carboxylic acid or $\beta$-
diketones, leading to the departure of alkoxy groups as follows:

$$
M(\text{OR})_z + x \text{XOH} \leftrightarrow M(\text{OR})_{z-x} (\text{OX})_x + x \text{ROH}
$$
Table 2 Gel times and solution pH for TEOS systems employing different catalysts. Pope and Mackenzie, J. of Non Cryst. Sol., 87, pp.185, 1986

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Concentration (mol.:TEOS)</th>
<th>Initial pH of solution</th>
<th>Gelation time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.05</td>
<td>1.90</td>
<td>12</td>
</tr>
<tr>
<td>HCl</td>
<td>0.05</td>
<td>0.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>92</td>
</tr>
<tr>
<td>HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.05</td>
<td>0.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>100</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.05</td>
<td>0.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>106</td>
</tr>
<tr>
<td>HOAc</td>
<td>0.05</td>
<td>3.70</td>
<td>72</td>
</tr>
<tr>
<td>NH&lt;sub&gt;4&lt;/sub&gt;OH</td>
<td>0.05</td>
<td>9.95</td>
<td>107</td>
</tr>
<tr>
<td>No catalyst</td>
<td>—</td>
<td>5.00</td>
<td>1000</td>
</tr>
</tbody>
</table>

<sup>a</sup> Between 0.01 and 0.05

Monovalent complexing XO⁻ species (acetates, β-diketones) often behave as bidentate (bridging or chelating) ligands, giving rise to an increase of the coordination number N. They are more strongly bonded and less hydrolyzable than the alkoxy groups. The new precursor therefore exhibits a higher coordination of the metal atom, a different molecular structure, and a reduced functionality. Its chemical reactivity is strongly modified, and complexed alkoxides are usually much less sensitive toward hydrolysis and condensation. Nucleophilic chemical additives are currently employed to stabilize highly reactive metal alkoxides and control the formation of condensed species.<sup>26</sup>

Titanium iso-propoxide reacts with acetic acid (AcOH = CH₃COOH). For a 1:1 ratio, a slightly exothermic reaction takes place, leading to a clear solution:

\[
\text{Ti(O-i-Pr)}₄ + \text{AcOH} \rightarrow \text{Ti(OAc)} \cdot \text{(O-i-Pr)}₃ + \text{i-PrOH}
\]
Acetate behaves as a bridging ligand. The coordination of titanium increases from four to six and oligomeric [Ti(O-i-Pr)$_3$(OAc)]$_n$ species are formed (n = 2 or 3), which is demonstrated by Figure 6.

Esterification occurs when more than 1 mol of AcOH is added. Acetic acid in excess reacts with alcohol molecules released during complexation providing the in situ generation of water and giving rise to more condensed species. Only molecular clusters are formed under these conditions. Hexameric species [Ti$_6$O$_4$(O-i-Pr)$_{12}$(OAc)$_4$] are actually obtained upon aging an equimolar mixture of AcOH and Ti(O-i-Pr)$_4$ in a closed vessel. Only two-thirds (x = OAc/Ti = 4/6) of the added acetic acid has been used for complexation. Some water is then provided via esterification reaction arising from acetic acid in excess. It leads to the slow hydrolysis of alkoxy groups that are replaced by oxo bridges. In the presence of an excess of water, all organic groups are removed and clear transparent titanium dioxide gels or sols are obtained.

Acetylacetone (acacH = CH$_3$—CO—CH$_2$—CO—CH$_3$) is currently used for the stabilization of alkoxide solutions. It reacts readily with Ti(O-i-Pr)$_4$, giving a yellow solution of Ti (acac)(O-i-Pr)$_3$. However, as acetylacetone behaves as a chelating ligand, only monomeric species are formed, in which Ti is fivefold coordinated. Condensation is observed when water is added. Alkoxy groups are hydrolyzed first. Strongly bonded complexing acacH group are not hydrolyzed, even with an excess of water (unless pH < 2).

There are a variety of ways to make titania sol. One of them is to make use of the chemical reaction between a salt of titanium and another solvable salt. The titania sol can be obtained by controlling the pH of the solution. Another method involves the hydrolysis of alcoholic solution of titanium alkoxides. The more popular method is to make the sol using the chemical polymerization.
Figure 6 Chemical modification of Ti(O-i-Pr)4 by acetic acid (CH₃COOH) and acetylacetone (CH₃—CO—CH₂—CO—CH₃) leads to the formation of [Ti(O-i-Pr)₃(OAc)]ₙ and [Ti(O-i-Pr)₃(acac)]. Livage, Sanchez and Babonneau, “molecular precursor routes to inorganic solids” in Chemistry of Advanced Materials: An Overview, edited by L.V. Interrante and M.J. Hampden-Smith, Wiley-VCH, Inc., 1998, Chapter 9, pp. 402.

Matijevic, Budnik and Meites reported the preparation and mechanism of formation of titanium dioxide hydrosols of narrow size distribution. This method involved aging at elevated temperatures highly acidic solutions of TiCl₄ which also contain Na₂SO₄. Particle modal diameters increase with the duration of aging and with the increasing concentration of sulfate ions at a given concentration of titanium (IV) ions. A chemical mechanism of particle formation and growth was proposed. It considered the hydrolysis of titanium ions and the formation of strong titanium-sulfate complexes that slowly decompose on heating to yield (hydrolyzed) titanium (IV) ions, which were used up in the particle growth.
Formation, packing, and sintering of monodisperse TiO$_2$ powders were examined by Barringer and Bowen \textsuperscript{35}. Monodisperse TiO$_2$ powders were synthesized by the controlled hydrolysis of dilute alcoholic solutions of titanium alkoxides. The state of powder aggregation in dispersion and powder packing in the green bodies strongly affected the sintering behavior. The sintering of uniformly packed powder compacts resulted in finegrained microstructures with >99\% of theoretical density at temperatures much lower than those required to sinter conventional TiO$_2$ powders.

Kamiya, Tanimoto and Yoko \textsuperscript{36} described the preparation of TiO$_2$ fibers by the chemical polymerization method from titanium tetra-iso-propoxide (Ti(O-i-C$_3$H$_7$)$_4$) which were used for spin coating. A variety of other sol recipes were reported with experimental procedure of shaping the sol being the same. The typical recipe in shaping TiO$_2$ sol is 1 : 7 : 5 : 0.80 in molar ratio for Ti(O-Pr)$_4$ : H$_2$O : EtOH : HCl. Ti(O-iPr)$_4$ was first mixed with half the above amount of EtOH, then water and HCl dissolved in the remaining EtOH was added dropwise to the Ti(O-iPr)$_4$-EtOH solution while stirring. The addition of the alcoholic solution of water and HCl was made so slowly that turbidity did not occur in the mixed solution. In general, 0.5 to 1.0 hr was needed to complete the preparation of a solution, depending on the solution composition. The solution was cooled by water during the above procedures.

Yang, Zhao and Feng et al. \textsuperscript{37} reported the preparation of hierarchically ordered oxides. Porous silica, niobia, and titania with three-dimensional structures patterned over multiple length scales were prepared by combining micromolding, polystyrene sphere templating, and cooperative assembly of inorganic sol-gel species with amphiphilic triblock copolymers. The resulting materials showed hierarchical ordering over several discrete and tunable length scales ranging from 10 nanometers to several micrometers. The respective ordered structures could be independently modified by choosing different mold patterns, latex spheres, and block
copolymers. The examples presented demonstrated the compositional and structural diversities that were possible with this approach. The schematic in Figure 7 illustrates the procedure that was used to fabricate materials with two-scale ordering. Gelation of a self-assembling sol-gel precursor solution was carried out in the confined space of a poly(dimethylsiloxane) (PDMS) mold. The precursor solution has the same composition as used in the preparation of mesoporous silica film—that is, expressed as molar ratios, 0.008 to 0.018 poly(ethyleneoxide)-b-poly(propyleneoxide)-b-poly(ethyleneoxide) (EO$_n$PO$_m$EO$_n$); 1 tetraethoxysilane (TEOS); 20 to 60 ethanol (EtOH); 0.01 to 0.04 HCl; and 5 to 10 H$_2$O. When Pluronic F127 (EO$_{106}$PO$_{70}$EO$_{106}$) was used as the structure-directing block copolymer species, a cubic mesophase resulted, whereas a hexagonal mesophase was obtained when Pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$) was used. This sol-gel mesophase chemistry has recently been extended to the preparation of diverse thermally stable mesostructured transition metal oxide, including Nb$_2$O$_5$, TiO$_2$, ZrO$_2$, WO$_3$, AlSiO$_{3.5}$, and SiTiO$_4$, by slowing the hydrolysis of inorganic chloride precursor species in alcohol solution.
Figure 7 Schematic diagrams of the molding methods used to fabricate hierarchically ordered structures on a substrate. (A) For patterning of mesoporous solids, a droplet of sol-gel-block copolymer precursor solution was compressed between the silicone mold and the substrate by applying a pressure of roughly $1 \times 10^5$ to $2 \times 10^5$ Pa. The high interfacial free energy of the solution caused the precursor to dewet the substrate where the mold and the substrate where the in contact. (B) A sequential process for producing hierarchical ordering over three discreet and independent length scales. Yang, Deng, Zhao et al., Science, vol. 282, pp. 2244-2246, 1998.
CHAPTER 3: EXPERIMENTAL PROCEDURE

In fabricating the photonic band gap materials of TiO$_2$, the process involves the design and fabrication of one, two or more-layer original samples, formation of the sol-gel, infiltration of the sol-gel into the samples, sintering of the infiltrated samples, characterization of obtained samples including the morphological and optical characteristics. Figure 8 shows the flow chart of the experimental procedure.

Figure 8 Flow chart of the experimental procedure
3.1 Design and Fabrication of One-, Two- and More Layer Samples

The master mold with a desired feature (it is relief in structure with the distance of 2.5 microns between neighboring bars and 0.5 micron bar width) was made at Microelectronics Research Center at Iowa State University. The two components (a resin and a hardener) for PDMS are mixed in a 10:1 ratio by weight until a uniform solution is achieved. This solution is poured onto the “master” mold, being careful to minimize air entrainment. The solution is allowed to cure in the master for half an hour at 65 °C. After cooling, the PDMS is carefully peeled away from the mold. This procedure must be done in a low dust environment.

The procedure for fabricating multi-layered samples is adapted from Xia, Zhao, and Whitesides 24 summarized in a previous section. The epoxy resin and the hardener are mixed together in a 10:3 weight ratio. Some of the prepolymer is placed on the patterned surface of the elastomeric mold (The elastomeric mold is prewarmed before coating with the epoxy). The whole system is allowed to cure at 65 °C for 5 min. It is necessary to repeat the above procedure for seven times in order to put enough epoxy on the surface of the pattern. The prepolymer is then fully cured thermally for four hours at 65 °C. Typically, the whole system is left overnight before the elastomeric mold is peeled off from the substrate. Similar procedures can be employed to fabricate two and more-layer samples according to the procedure described in the previous work. In making multi-layer samples, the alignment of the epoxy layer is done under the microscope of Kar Suss MJB 3 UV 300 mask aligner. The mask aligner has a rotation and translation stage for fine angle and lateral alignment.
### 3.2 Formation of the Sol-gel

Sol-gel infiltration of the sample is used to create the desired TiO$_2$ structure. Infiltration must occur before gelation occurs. If gelation occurs before or during infiltration, the viscosity will be too high and the result is incomplete infiltration. A number of different precursors can be used. Other variables include the pH, addition sequence, gelation, the ratio of precursor to water, the ratio of precursor to water, and the ratio of precursor to alcohol, different alcohols, and different catalysts. The following precursors have been studied: titanium diisopropoxide bis (2,4-pentadionate) (TDBP, 75wt% and 25% isopropanol), tetraethyl orthotitanate (TEOT)(the concentration is ~20% but 80% for titanium isopropoxide (TIPP)), and titanium isopropoxide (~97% of concentration), Ethanol (100 wt%) and isopropanol (99.99 wt%) have been used for the alcohol and hydrofluoric acid (HF, ~49 wt%), hydrochloric acid (HCl, 37.4 wt%), hydriodic acid (HI, 47 wt%) have been examined as the catalyst.

A variety of preparation procedures are possible with TDBP. One such procedure is as follows. The isopropanol (99.9 wt%) is added to a clean dry container. Then TDBP (75 wt%) is added and stirred with a magnetic stirrer until uniform and allow the solution to cool. Two drops HCl (37.4 wt%) is added into the above solution while stirring. The water is slowly added to the solution dropwise in 15 min or 20 min while stirring. A typical recipe for the sol of TDBP is: 2 mol% : 89 mol% : 9 mol% between TDBP, isopropanol and water.

The preparation of the sol of TEOT and TIPP varies from that of TDBP. Using a similar procedure, half of the ethanol (100 wt%) is added into a clean container. Then the precursor TDBP or TIPP is added to the pure ethanol. The mixture has to be uniform and to be cooled before next step can occur. The remaining half of ethanol is added to another container. The needed water is added into the container with the remaining half of the ethanol and HCl is also added to this solution. Then the container is shaken to make sure that the solution is
uniform and cooled. A syringe is used to transfer the solution with ethanol, water and HCl and added to the solution with ethanol and precursor drop by drop in at least half an hour or one hour (typically around 45min). For the sol of TEOT, the addition of first couples of drops may cause the solution with ethanol and precursor to be turbid. When this occurs, the addition is continued until the solution become transparent. For the sol of TIPP, the solution with ethanol and precursor is always transparent. A typical recipe is such that the mole ratio between TEOT, ethanol, water and HCl is 2.13%: 29.79%: 63.83%: 4.25%.

Another method may be used to obtain the sol of TEOT or TIPP. It is basically the same as the one in TDBP. However, since the different organic group (ethyl) occurs, the precipitation may take place very quickly depending upon the concentration of alcohol and the addition sequence. Compared with the former procedure for the preparation of the sol of TEOT or TIPP, the latter is not preferred.

3.3 Infiltration of Sol-gel into the Sample

There are several methods that can be utilized to infiltrate the sample with sol-gel. One of them is to put a drop of sol directly on the top of the sample then let it dry naturally. Another method involves using capillary suction to draw the sol-gel into the pattern. The procedure is as follows. A drop of sol is put near one edge along the direction of patterning (there are two edges for a one-layer sample and four edges for a two-layer sample) and then the sample is kept erect by using a plastic frame to facilitate infiltration of the sol into the pattern along the direction of patterning. The whole system is quickly put into a closed chamber with a humidity of 95% and allowed to dry slowly. Another method is spin coating, which involves placing several drops of the sol on the surface of the sample and spinning at 3,000 rpm for one minute.
3.4 Heat Treatment and Sintering

Heat treatment is required to remove the epoxy pattern, to convert the pre-ceramic polymer to TiO$_2$, and to densify the resulting ceramic. The heat treatment procedure is shown in Table 3. This procedure is designed to minimize cracking during shrinkage.

3.5 Characterization of Samples

The characterization of the sample before and after sintering is necessary to elucidate the effect of defects in original patterns, the changes occurring during sintering, the distribution of TiO$_2$, and the optical properties. An optical microscope was used to examine the pattern before sintering. The scanning electron microscope (SEM) was used to inspect the structure, and to determine the distribution and morphology of titania after sintering. Optical transmission spectra were collected to elucidate the location, width and depth of the photonic band gap.

Table 3 Heat treatment procedure

<table>
<thead>
<tr>
<th>RAMP TIME (HR)</th>
<th>SOAK TIME (HR)</th>
<th>RUN-DOWN (HR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>From room T to 550 °C</td>
<td>550 °C</td>
<td>From 550 °C to room T</td>
</tr>
</tbody>
</table>
CHAPTER 4: RESULTS AND DISCUSSION

4.1 Design and Fabrication of One-, Two-, and More-layer Samples

An elastomeric PDMS plastic mold is produced from the "master" mold with desired features. While fabricating the plastic mold, one critical step is to keep it from absorbing air and to keep the system very clean because the existing dirt may give rise to defects in resultant samples when the one- or two-layer sample is shaped. In the preparation of multi-layer samples, it is preferred that there is no excess epoxy used in the process. Otherwise, the epoxy patterns, especially for the upper layer will be overfilled. On the other hand, too little epoxy will result in broken lines in the sample and in the titania pattern created from it, which can destroy its photonic properties. In addition, when the formation of two-layer sample is complete, the sample should be left undisturbed for at least two days before it can be used for infiltration to ensure the epoxy has fully cured. In this case, the sample can be put into an oven at elevated temperature to allow it to cure more. The partially cured epoxy pattern may swell or deform if the infiltration of the sol-gel into the sample is done. At this stage, the uncured epoxy group is very sensitive to alcohol and water and therefore the chemical reactions may occur. The resulting swelling or deformation may also destroy the end photonic performance. Very good one- and two-layer samples had been obtained. The optical micrographs for one- and two-layer sample appear in Figure 9. These two pictures clearly show that we can produce pretty good one- and two-layer samples. As a matter of fact, almost four-layer and eight-layer samples have been produced in our lab by stacking two two-layer samples and two four-layer samples, respectively. The quality of the four- and eight-layer sample depends largely upon the original two-layer and four-layer samples. Also, the technique of stacking plays an essential role in producing high-quality multi-layer samples.
4.2 Formation of the sol-gel

Sol-gel processing is an effective way to produce a ceramic with fine features. Three precursors have been explored to make a sol. The different organic groups in the three precursors determine their gel times and therefore have distinct processing procedures.

Since the precursor of titanium diisopropoxide bis (2, 4-pentadionate) (TDBP, 75wt% and 25% isopropanol) has different organic groups from tetraethyl orthotitanate (TEOT)(the concentration is ~20% but 80% for titanium isopropoxide (TIPP)), and titanium isopropoxide (~97% of concentration), the sol of TDBP exhibits a very long gel time and has more flexible recipes with alcohol and water. With the precursors of TEOT and TIPP, they are very similar to each other (there are little difference between ethyl and isopropyl groups compared with those between 2, 4-pentadionate and ethyl or isopropyl group) and demonstrate that they are very sensitive to water. When the sol of TEOT or TIPP is produced, pure ethanol (100%) must be used. Otherwise, precipitation of TiO$_2$ occurs immediately upon adding ethanol into the
precursor. The pH of the sol plays a significant role in determining whether the precipitation of TiO₂ occurs or not. The pH of the sol from TEOT or TIPP is recommended to be around 1.0 to ensure that the precipitation of TiO₂ does not take place. The catalyst basically accelerates the chemical reaction. Three catalysts, HF, HCl and HI have been employed. It was demonstrated that the sol with HI has a much longer gelation time than the one with HF or HCl, especially the former. This can be attributed to the fact that I⁻ ion has a much bigger radius compared with F⁻ and as a result gives rise to a big steric hindrance in the formation of gel. This effect is only obvious for the sols of TEOT and TIPP. Additionally, since a slide glass is used as the substrate, using HF as a catalyst may erode the substrate and therefore HF should not be used here. For HI, I⁻ is brown and although it is probable that I⁻ evaporates at elevated temperature, it is not clear whether any I⁻ will remain in the sample. As a result, HI is not recommended for use. In the combination of the effects, HCl is preferred as a catalyst.

As it is indicated in the previous chapter, different procedures are used in making the sol of TDBP and the sol of the TEOT or TIPP due to the fact that different precursors are used. For making the sol of TDBP, some experimental details are of more importance so that a good transparent solution can be obtained. When the sol of TDBP is made, the isopropanol (99.99%) must first be added into the container, followed by the addition of the precursor of TDBP. This procedure can not be inverse. Otherwise precipitation along the wall of the container may take place. Similar phenomenon can definitely occurs for the system of TEOT or TIPP with ethanol somehow if this procedure is inverse. In making the sol of TEOT or TIPP, a specific experimental procedure called two-step approach is employed with the consideration of the nature that the precursor of TEOT or TIPP is pretty sensitive to water and pH of the solution. By using this approach, more flexible recipes for the sol of TEOT or TIPP can be successfully obtained.
4.3 Infiltration of Sol-gel into the Sample

The challenge of infiltration is in both the extent of infiltration and in the quantity of titania deposition. For the capillary approach, although the end epoxy pattern can densify by multiple infiltration, it is experimentally difficult for one to obtain a large good area of TiO$_2$ with desirable uniformity because the sol dries too fast to go in so far. Also, owing to multiple infiltration, the edges of the epoxy pattern are subjected to swelling or deformation because the uncured epoxy groups may exist and they can react with water, alcohol and byproduct alcohol resulting from the reactions. Experimentally, the sol of TDBP dries in ten minutes or less, even though it is put in a closed chamber with a humidity of 95%. With the spin coating approach, a infiltrated sample with high uniformity and larger good areas can be achieved, compared with the case using capillary approach, depending on the nature of sol, the concentration of precursor in the sol, the spin speed, and the spin time. For the sol from a precursor, the larger organic groups the precursor contains, the longer the gelation time. Thus, considering all the factors involved, we may optimize spin-coating conditions. Furthermore, it is unknown whether the spin coating accelerates the chemical reactions involved. While the spin coating is going on, sometimes the swelling or deformation of the epoxy pattern occurs. However, sometimes it does not occur. Swelling does not occur for TDBP spin coated on samples that had cured for a long time (>1 week). However, for most TDBP samples, swelling or deformation is evident. For the sol of TEOT or TIPP, in any case, swelling or deformation of epoxy patterns rarely occurs. It has been shown that acetylacetone (acacH=CH$_3$—CO—CH$_2$—CO—CH$_3$) does swell the epoxy pattern a little bit. Still, it is unknown that how the amount of acac affects the epoxy because the amount of byproduct from the chemical reaction is fairly small compared to the amount used to show acac swells the epoxy. Therefore,
it may be supposed that there may exist the unhardened (uncured) epoxy groups that can be swellable to the byproduct acac, alcohol and water.

4.4 Heat Treatment and Sintering

Heat treatment and sintering of the infiltrated samples involves the gelation, drying, aging of gels, consolidation, and densification. Generally, this includes the transitions from sol to gel and from gel to ceramic. The hydrolysis and condensation reactions within the sol lead to the growth of clusters that eventually collide and link together into a gel. The chemical reactions that cause gelation continue long after the gel point, producing strengthening, stiffening, and shrinkage of the network. The driving forces for shrinkage include chemical effects, such as condensation reactions, and physical effects, such as capillary pressure. Fluid transport can occur by flow down a pressure gradient or diffusion down a chemical potential gradient and deformation of the network may involve elastic, plastic, or viscoelastic strains.

It has been demonstrated that the shrinkage of gels during aging is attributable to ongoing condensation reactions between M-OH groups. The total contraction resulting from condensation can be enormous. If the evaporation is permitted during aging, the contraction can shrink several times. Thus, the driving force for shrinkage provided by chemical reactions is small compared to the other factors operating during evaporation. Moreover, organic groups that adsorb or chemisorb on the M-OH groups inhibit condensation and thereby further reduce the influence of chemical reactions on shrinkage. The driving force for shrinkage during drying of a gel includes stresses produced by chemical reactions, as well as osmotic, disjoining, and capillary forces. Usually the most important of these is the capillary force arising from the difference between the solid-vapor and solid-liquid interfacial energies. The huge interfacial area of gels (~300-1000 m²/g) can result in capillary pressures as large as ~100MPa. These
driving forces produce compressive stresses that draw the solid network into the liquid (so there is a flux of solid through the liquid). Structural changes during heating can be divided into three stages that account for shrinkage. The first stage involves weight loss with little shrinkage. The second stage deals with both substantial weight loss and substantial shrinkage. The third stage is related to shrinkage with little weight loss. The weight loss in first stage corresponds to the endotherm attributed to desorption of physically adsorbed water (or perhaps residual solvent) whereas concurrent weight loss and shrinkage in second stage can be attributed primarily to removal of organics (principally weight loss), polymerization (shrinkage $\propto$ weight loss), and structural relaxation (shrinkage only).

Sintering is a process of densification driven by interfacial energy. When the minimum of interfacial energy reaches, the densification stops.

### 4.5 Characterization of Samples

Optical microscopy and scanning electron microscopy are useful to inspect the structure, morphology of titania. Similarly, optical transmission spectra measured are to elucidate the location, width and depth of the photonic band gap. Figure 10 illustrates the morphology and structure of sintered 2-layer samples from the sol of TDBP, TEOT and TIPP by spin coating, respectively. Figure 11 shows the optical morphology and structure of 3-layer sintered sample form from the sol of TDBP by spin coating (three spins).

Figure 12 shows the cross section of a 2-layer epoxy pattern without infiltration. Figure 13 shows the SEM micrographs for a sintered 1-layer sample with the infiltration from the sol of TDBP (6 wt %) by capillary approach. Figure 14 and Figure 15 demonstrate morphological and structural features by SEM for a sintered 2-layer samples from the sol of TDBP and the sol of TEOT by spin coating, respectively. Figure 16 illustrate the morphological and structural
Figure 10 Optical micrographs for sintered 2-layer samples (a) from sol of TDBP (b) from the sol of TEOT and (c) from the sol of TIPP by spin coating. (a) 1,000 X (b) 1,000 X and (c) 1,000 X.
Figure 11 Optical micrograph for a sintered 3-layer sample with the infiltration of TDBP by spin coating (three spins). 1,000 X.

Figure 12 SEM micrographs of cross section of a 2-layer sample with epoxy. (a) 6,500 X (b) 6,500 X.
Figure 13 SEM micrographs for a sintered 1-layer sample with the infiltration from the sol of TDBP by the capillary approach. (a) 1,700 X (b) 3,000 X (c) 5,000 X (d) 15,000 X.
Figure 14 SEM micrographs for a sintered 2-layer sample with the infiltration of the sol of TDBP by spin coating. (a) 850 X (b) 1,500 X (c) 5,000 X (d) 22,000 X.
Figure 15 SEM micrographs for a sintered 2-layer sample with the infiltration of the sol of TEOH by spin coating. (a) 600 X (b) 1,900 X (c) 7,500 X (d) 12,000 X.
Figure 16 SEM micrographs of the cross section of a sintered 2-layer sample with the infiltration of the sol of TDBP by spin coating. (a) 4,500 X (b) 7,000 X (c) 17,000 X (d) 22,000 X.
characteristics of the cross section of a sintered 2-layer sample with the infiltration of the sol of TDBP by spin coating.

Figure 17 and Figure 18 demonstrate the FTIR spectra for a sintered 2-layer sample with the infiltration of the sol of TDBP (12 wt%) by spin coating (TiO$_2$ and Si as reference) and the FTIR spectra for a sintered 4-layer sample with the infiltration of the sol of TDBP (26 wt%, six spins) through spin coating, respectively.

Figure 19 demonstrates the morphological characteristics for the cross section of a sintered 2-layer sample with the infiltration of the sol of TDBP (26 wt%) through spin coating on a slide glass. Figure 20 shows the morphological features for a sintered 2-layer sample with the infiltration of the sol of TDBP (26 wt%) through spin coating on a slide glass. This sample was sintered with the pattern facing down in a furnace. Figure 21 illustrates the morphological and structural features for a sintered 4-layer sample with the infiltration of the sol of TDBP through spin coating. Six spins were used — five spins with the sol of TDBP (26 wt%) and one spin with the sol of TDBP (12 wt%). That sample was sintered with the pattern inverted as well.

From Figure 13, it is clear that with the capillary approach, it is possible to get a more compacted one-layer sample with multi-infiltration because the width of one bar is close to one micron, the size of the channel in the mold. Thus, it appears that shrinkage is limited. For spin coating, a 2-layer samples can be obtained with a big shrinkage (~up to 40%) and a large area. This large shrinkage results from several factors. One of them may be attributable to the low concentration of the precursor in the sol. Another factor might be due to the fact that there may exist a concentration gradient of the sol normal to the film plane.
Figure 17 FTIR spectra for a sintered 2-layer sample with the infiltration of the sol of TDBP by spin coating with TiO$_2$ and Si as reference.

Figure 18 FTIR spectra for a sintered 4-layer sample with the infiltration of the sol of TDBP(six spins in which five is for 26 wt% of the sol and one for 12 wt% of the sol on a silicon wafer) by spin coating with TiO$_2$ and Si as reference.
Figure 19  SEM micrographs of the cross section of a sintered 2-layer sample with the infiltration of the sol of TDBP (26 wt%) by spin coating on a slide glass. (a) 1, 900 X (b) 7, 000 X (c) 12, 000 X.
Figure 20 SEM micrographs of a sintered 2-layer sample with the infiltration of the sol of TDBP (26wt%) by spin coating on a slide glass. (a) 750 X (b) 1,900 X (c) 7,500 X (d) 15,000 X.
Figure 21 SEM micrographs of a sintered 4-layer sample with the infiltration of the sol of TDBP (six spins in which five is for 26 wt% of the sol and one for 12 wt% of the sol on a silicon wafer). (a) 10,000 X, tiled at 20° (b) 10,000 X, tilted at 45° (c) 8,000 X, tilted at 30° (d) 15,000 X at 30°.
From the pictures for cross section of the sample, it has been further proven that there is little material there (TiO$_2$). However, in order to explore why little material appears in the sintered structure, the morphology of cross section of the original uninfiltreted epoxy pattern had been investigated. In addition, the sol of TDBP with higher concentration (26 wt %) was used to probe whether increasing the concentration of the precursor in the sol can result in the expected “bridge” structure between the upper and the lower layers. From Figure 12, the height of the upper layer approaches around 0.8-0.9 micron. Thus, we can exclude the possibility that it is due to the very small height of the original pattern that brings about the low material of TiO$_2$. The SEM micrographs from Figure 19 and 20 clearly show that the increase on the concentration of the precursor in the sol can enhance the material of TiO$_2$ in the patterned structure with one spin.

Although increasing the concentration of the precursor in the sol tends to give rise to more dense structure of TiO$_2$, that concentration should not be so high that overfilling or cracking occurs during infiltration or sintering. Furthermore, that concentration might depend on different samples. For example, experimentally, the infiltration of using the sol of TEOT or TIPP with the concentration of 42wt% on a 2-layer sample can result in cracking because the pattern is overfilled. In another word, the sol of TEOT or TIPP with a concentration of 42wt% does not work for the 2-layer sample. But for 3-layer, 4-layer or other multi-layer samples, the sol of TEOT or TIPP with a concentration of 42 wt% may work. A good sintered 4-layer sample was obtained by infiltrating the sol of TDBP six spins through spin coating. The sol of TDBP with a concentration of 26 wt% was infiltrated five times but once for the sol of TDBP with a concentration of 12 wt%. No cracking or swelling occurred. From the above experiments on the 4-layer sample, it can be supposed that the sol of TDBP with a
concentration of 40 wt% may work. So far, the investigation on the infiltration of the sol to 4-layer or other multiple-layer samples has been insufficient.

The FTIR spectra show that there is a strong peak or dip in transmission around 1500 cm\(^{-1}\). However, compared with that of slurry, there is an additional peak around 2350 cm\(^{-1}\). It remains unclear what it is. Also, it can be suggested that the spectra result not only from the photonic band gap structure but also from titania itself. Therefore, the absorption from titania itself must be removed so that the photonic band gap structure information can be obtained. Since there is not enough material (TiO\(_2\)) in the structure, which actually changes the filling ratio and cause a shift of band gap, there may exist a shift with respect to band gap between the measured and theoretical value. It is still unknown how much the shift is. FTIR spectra for a sintered 4-layer sample are very similar to those from a sintered 2-layer one. The difference between them lies in the width of the peaks arising from different polarization. Also, the peak around 2800 cm\(^{-1}\) in 4-layer sample looks evident which is involved in the second band gap. Yet in the spectra of 2-layer sample, this peak disappears.

Certainly one of the most technologically important aspects of sol-gel processing is that, prior to gelation, the fluid sol or solution is ideal for preparing thin films by such common processes as dipping, spinning, or spraying. It has been argued that spin coating could be divided into four stages: deposition, spin-up, spin-off, and evaporation, although evaporation may accompany the other stages. An excess of liquid is dispensed on the surface during the deposition stage. In the spin-up stage, the liquid flows radially outward, driven by centrifugal force. In the spin-off stage, excess liquid flows to the perimeter and leaves as droplets. As the film thins, the rate of removal of excess liquid by spin-off slows down, because the thinner the film, the greater the resistance to flow, and because the concentration
of the nonvolatile components increases raising the viscosity. In the fourth stage, evaporation takes over as the primary mechanism of thinning.

An advantage of spin coating is that a film of liquid tends to become uniform in thickness during spin-off and, once uniform, tends to remain so provided that the viscosity is not shear dependent and does not vary over the substrate. This tendency arises due to the balance between the two main forces: centrifugal force, which drive flow radially outward, and viscous force (friction), which acts radially inward. During spin-up, centrifugal force overwhelms the force of gravity, and the rapid thinning quickly squelches all inertial forces other than centrifugal force. The thickness of an initially uniform film during spin-off is described by:

\[ h(t) = \frac{h_0}{\left(1 + 4\rho\omega^2 h_0^2 t/3\eta\right)^{\frac{1}{2}}} \]

Where \( h_0 \) is the initial thickness, \( t \) is time, and \( \omega \) is the angular velocity; \( \rho \) and \( \omega \) assumed constant. Even films that are not initially uniform tend monotonically toward uniformity, sooner or later following the above equation.

The spinning procedure creates a steady forced convection in the vapor above the substrate that causes the mass transfer coefficient, \( k \), to be quite uniform. Thus the evaporation rate in spin coating tends to be quite uniform also. A spun film arrives at its final thickness by evaporation after the film becomes so thin and viscous that its flow stops. According to a model of spin coating by Meyerhofer that separates the spin-off and evaporation stages, the final thickness and total elapsed time to achieve this thickness are:

\[ h_{\text{final}} = \left(1 - \frac{\rho_0}{\rho_\infty}\right) \left(\frac{3\eta e}{2\rho_0 \omega^2}\right)^{\frac{1}{2}} \]
and

\[ t_{\text{final}} = t_{\text{spin-off}} + h_{\text{spin-off}} \rho_0 A / e \rho_A \]

Where \( \rho_A \) is the mass of volatile solvent per unit volume, \( \rho_0 \) is its initial value, and \( e \) is the evaporation rate that depends on the mass transfer coefficient \( m \). All the three equations pertain to Newtonian liquids that do not exhibit a shear rate dependence of the viscosity during the spin-off stage.

Although the above equations were used to estimate and to calculate the thickness of the film during spin coating of the sol-gel, they cannot be completely applicable to calculate the film thickness in our experiment because initially the film is formed by infiltration on a specific substrate with a specific geometry. In this case, the substrate is a film with a relief structure. This film looks like flat but actually it is not. However, all the above three equations assume that the film may shape on a flat surface. Particularly, the thickness of the film from sol-gel by spin coating should not be more than one micron, the theoretical value of the original thickness. Otherwise, cracking definitely takes place during heat treatment and sintering because much more sol-gel can result in much more stress when condensation and evaporation occur which finally cause the transition from liquid to solid phase with heat treatment and sintering going on and on. Still, those equations are able to give us some insight on the thickness of the film especially when this thickness is less than one micron.

In order to get a better understanding on structural development, exploration of how the liquid coating become solid is essential. The hydrolysis and condensation reactions that cause gelation in the bulk are also at work in coating to increase molecular weight of the precursor. However, in coatings the evaporation of solvent and other volatiles makes the composition, and thus the reactions rates in the coating dynamic, changing with time and depth into the coating.
Reactions lead to gelation, but physical processes, such as aggregation and entanglement, can also drive solidification. The solidification behavior should be influenced by drying conditions, precursor structure and reactivity, regardless of origin. Also, drying affects gelation. Early in the process, the molecular weight is fairly constant; however, as time elapses the molecular weight at the coating surface grows. Drying increases the concentration of alkoxide precursors at the surface, accelerating reactions there. Eventually, the molecular weight diverges to infinity and a “gel” is formed. For this combination of reaction and drying conditions, the coating surface gels first, forming a “skin”. When the drying rate is low or the coating is thick, reactions that lead to gelation occur quicker than evaporation, and the coating gels before it dries. When the reactions are slow or the coating is thin, drying is faster and less time is available for reaction; therefore, these coatings dry before they gel or they do not gel at all if water is evaporated.

The competition between evaporation and condensation in establishing the coating microstructure should also be considered. Evaporation and attendant capillary forces compact the structure, while condensation reactions stiffen the gel network and cause greater resistance to flow. The relative rates of these two processes are influenced by the properties of the solution precursor and the deposition conditions. Factors that increase the condensation rate in bulk gels should have a like effect on coatings. For instance, greater amounts of water and use of a base additive produces coatings which have higher condensation rates; these coatings become rigid gels before evaporation compacts the structure and are therefore more porous.

The densification of titania coatings was probed by Keddie et al. They prepared films by spin coating solutions of titanium ethoxide in t-butyl alcohol. Figure 22 shows the shrinkage for coating heated at 60 °C/min and 8000 °C/min (by rapid thermal annealing). The coatings initially shrink at constant rate (region I). Then, shrinkage levels somewhat and again
Figure 22 Shrinkage as a function of temperature for titania sol-gel derived coatings heated at 60 °C/min (O) and 8000 °C/min (Δ). Keddie, Braun and Giannelis, Interrelationship between densification, crystallization, and chemical evolution in sol-gel titania thin form, J. American Ceramic Society, 77(6), pp. 1592-1596, 1994.

increases at a constant rate (region II), eventually reaching a plateau (region III). Chemical analysis (for hydrogen and carbon) revealed that continued condensation reactions between hydroxyl groups were responsible for shrinkage in regions I. Region II shrinkage was due to the combined effects of structural relaxation and condensation. At high heating rates, the amount of condensation induced shrinkage was less, but the structural relaxation induced shrinkage was greater and coating were more dense. Structural relaxation was greater because a less crosslinked, lower viscosity structure is retained to higher temperatures when faster heating rates are used. The arrest in shrinkage, as noted by the plateau, was due to the formation of a significant amount of crystalline titania. Higher heating rates shifted the crystallization to high temperatures and allowed more densification.

Vorotilov et al. 47 reported that shrinkage in sol-gel derived titania coating increased with increasing concentration of alkoxide in the coating solution and with decreasing R_h which
was defined by $R_h = [\text{H}_2\text{O}]/[\text{M}]$, where M is the metal cation in the alkoxide. In our case, we use a three-step heating procedure in which the heating rate is close to 0.43 °C/min. Therefore, the shrinkage in our experiment should be less than the one in Figure 22 if other factors are the same because the low heating rate can cause low structure evolution and uniform structures. The above relationship between shrinkage and heating rate is able to offer us some insight on the shrinkage of titania. In fact, the horizontal shrinkage in our structure of titania ranges from 10% to 40% depending on the precursor, the chemistry of sol-gel. At present, it is hard to draw a conclusion on how much the normal shrinkage is because we can not make sure whether the pattern is exactly filled or not even though the pattern is partially filled. Undoubtedly, shrinkage may be the largest challenge in our approach, as we know that the low filling ratio resulting from enormous shrinkage will change the optical property of the structure of titania.

The tremendous changes in structure that a sol-gel coating experiences during processing, together with the constraint placed on the coating by the substrate, lead to the development of stresses. In the beginning, the coating changes from a viscous liquid to an elastic solid; stress arise from the strain that develops as the coating takes on a configuration that departs from its local stress-free state. The local stress-free state changes during processing in response to local concentration changes (from solvent evaporation), composition and structure changes (from reaction), and temperature changes (from thermal treatment) and is dependent on the history of the process. To relieve stresses, the material can relax internally by molecular motion or it can deform, taking on a new shape closer to the stress-free state. Internal relaxation slows as the material approaches an elastic solid and deformation is restricted by adherence to the substrate. Since the stress-free state shrinks during solidification and adherence to the substrate confines shrinkage in the coating to the thickness direction, in-plane tensile stresses result. Adherence to the substrate also brings about peeling and shear
stresses near the coating edges. As the coating is heated, stresses can become more severe as additional strain develops from pyrolysis of bound organics, crystallization, phase transformations, and solid state sintering. During heating and cooling, thermal expansion mismatch with the substrate also contributes to stress.

Cracking is one form of stress relief. Cracks can develop at any stage of the process and limit the coating thickness (usually < 1 µm). Whether or not a crack forms depends on the magnitude of the stress, the thickness of the coating, materials properties, and perhaps the presence of a void or flaw. Materials properties and stress evolve during processing, and the thickness is continually changing. As far as the stress and cracking in our experiments are concerned, the defects in the initial pattern and the overfilling arising from more sol-gel with a higher concentration and multi-spin should be paid more attention. Actually, some kinds of defects in the original epoxy pattern such as broken lines and dusts exist especially around the edges. Those defects may give rise to local stresses during heat treatment, which finally brings about deformation and irregularity or discontinuity of the pattern. Those defects and the adverse effects arising from them should be minimized even though some very good sintered areas of the pattern can still be found out around the center of the sample. A large defect free area is required for good optical measurements. In our experiment, cracking may take place during infiltration or heat treatment. Cracking does not only occur in the pattern, but can also result in excess TiO$_2$ on the surface of the pattern from overfilling. Cracks in the pattern are fairly rare. In spin coating, cracking never happened. Undoubtedly, cracking arising from overfilling can be avoidable if the infiltration of the sol-gel gets under control. On the other hand, to obtain a more dense patterned area of TiO$_2$, the original epoxy pattern should be filled but not overfilled. Thus, this process must be optimized. It is indicated in the DSC and DTA experiments that epoxy may crystallize around 184 °C. Significant crystallization enables the
original pattern to be deformed. The experiment shows that there is no deformation when the original epoxy pattern is heated up to 200 °C. Thus, the stress or deformation associated with the crystallization of epoxy can be ignored.
CHAPTER 5: CONCLUSIONS

This work has investigated the fabrication of 1D, 2D and 3D PBG structures of TiO$_2$ by using microtransfer molding and sol-gel processing. Both the capillary approach and spin coating can be used to infiltrate the sol-gel into the epoxy pattern regardless of the substrate. There is difficulty completely infiltrating samples through capillary action. The sol tends to dry too quickly preventing further infiltration. Spin coating is a viable method to obtain a uniform sample with large regions. The optimal conditions for spin coating have not yet been obtained.

Titanium diisopropoxide bis (2, 4-pentadionate)(TDBP), tetraethyl orthotitanate (TEOT) and titanium isopropoxide (TIPP) have been successfully used to make a sol-gel. TDBP has a flexible range of recipe considering the pH, addition sequence, the ratio between water and alcohol, and the ratio between water and precursor compared with precursors of TEOT and TIPP. The sol of TEOT or TIPP can only be made under the condition that it has very low pH and a specific addition sequence of precursor, alcohol, water and catalyst. The sintered samples from the infiltration of the sol from TDBP look better than those from the sol of TEOT or TIPP. Heating ramps with three steps were used to minimize the cracking during heating.

The 2D sintered samples from the sols of TDBP, TEOT, TIPP with the concentration for precursor of 12 wt% by spin coating have low TiO$_2$ in structures and experience a huge shrinkage (up to 40%). A sintered 4-layer sample was successfully obtained with the infiltration of the sol of TDBP (26 wt%).

FTIR spectra show that there exists a stronger peak around 1500 cm$^{-1}$ which may be related to the first band gap.
CHAPTER 6: FUTURE WORK

Spin coating is a viable method to fabricate a 2-layer sample either using the sol-gel of TDBP or the sol-gel of TEOT. However, the sol-gel of TDBP or TEOT sometimes swells the epoxy pattern. The causes and avoidance of swelling must be determined ensuring there is no deformation of TiO$_2$ in samples. Still, the optimal operational conditions including spin speed, spin time, how many spins are needed remain unclear. Much more work could focus on these issues. The precursors of TDBP and TEOT have different organic groups, and the operational conditions are likely to be different. Further work should investigate these effects.

Another problem that remains is the issue of the very low filling ratio. Further effort could be made to explore increasing the concentration precursor of the sol of TDBP or TEOT. So far, the concentration of the precursor in the sol is around 12 wt%. Moreover, more spins can be used. For example, we can give the sample twice or three times spins instead of once spin. More efforts could be made here.

Although a sintered 4-layer sample is obtained, the optimum processing conditions on spin coating remain unclear. The processing conditions on spin coating may be different from those in one-layer and two-layer. Therefore, more investigation could be made to address the problems. Also, more efforts in improving the filling ratio for 3D structures can be made. More work on reflection and transmission to the sample could be done to further address the band gap information.
APPENDIX A: CHEMICALS AND EQUIPMENT USED

The following is the description on the chemicals and equipment in the experiment.

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<th>Chemical name</th>
<th>Concentration</th>
<th>Chemical formula</th>
<th>Company</th>
<th>Comment</th>
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</thead>
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<tr>
<td>TDBP†</td>
<td>75%</td>
<td>$C_{16}H_{28}O_6Ti$</td>
<td>Acros Organics</td>
<td></td>
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<tr>
<td>TEO†</td>
<td>80%</td>
<td>$C_{8}H_{20}O_4Ti$</td>
<td>Fluka Chemie AG</td>
<td></td>
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<tr>
<td>TIPP*</td>
<td>97%</td>
<td>$C_{12}H_{28}O_4Ti$</td>
<td>Chemat Tecnology, Inc</td>
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<tr>
<td>2-propanol</td>
<td>99.99%</td>
<td>$C_3H_8O$</td>
<td>Fisher Scientific</td>
<td></td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>100%</td>
<td>$C_2H_6O$</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Acetyl acetone</td>
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<td>$C_5H_8O_2$</td>
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</tr>
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<td>hydrochloric acid</td>
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<td>HI</td>
<td>Fisher Scientific</td>
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<tr>
<td>Acetic acid</td>
<td>100%</td>
<td>$C_2H_4O_2$</td>
<td>Fisher Scientific</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
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<th>Equipment</th>
<th>Brand/Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo-resist spinner</td>
<td>Headway Research, Inc.</td>
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<tr>
<td>PDMS*</td>
<td>Dow Corning Sylgard 184 silicone elastomer</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Tra-Bond BA-2115 by Tra-Con</td>
</tr>
<tr>
<td>FTIR</td>
<td>Nicolet System 760</td>
</tr>
<tr>
<td>Optical microscope</td>
<td>Olympus BH2-UMA</td>
</tr>
<tr>
<td>Scanning electron microscope</td>
<td>JEOL 6100</td>
</tr>
</tbody>
</table>
TDBP\textsuperscript{\dagger}: titanium diisopropoxide dis(2,4-pentanedicarboxylate) 75wt\% in 2-propanol.

TEOT\textsuperscript{\circledast}: tetraethyl orthotitanate \sim 20\% tetraisopropyl orthotitanate.

TIPP\textsuperscript{*}: titanium isopropoxide.

PDMS\textsuperscript{*}: poly(dimethylsiloxane).
APPENDIX B: CALCULATIONS OF THE RECIPE

The following are the calculations of the recipe for the sol of TDBP, TEOT and TIPP.

Calculate the recipe for the sol of TDBP

Recipe: TDBP: isopropanol:water = 2mol%: 89mol%: 9mol% (it is assumed that 0.45 gram of pure TDBP is needed)

TDBP: 0.6×0.75 =0.45 g (0.6-0.45=0.15 isopropanol)

\[
\frac{0.45}{364.3} = 1.2352 \times 10^{-3} \text{ mol}
\]

Total mole number = 1.2352×10^{-3} /2mol% = 0.06176 mol

Isopropanol: 0.06176×0.89×60.1= 3.3035 g

3.3035- 0.15 = 3.1535 g

Water: 0.06176 ×0.09× 18 = 0.1005 g

HCl = 1–2 drops

TDBP wt%=11.68%, isopropanol wt%= 85.72% , water wt%= 2.6%

Calculate the recipe of the sol of TEOT

Mole ratio: TEOT: water: EtOH: HCl = 0.5: 7: 15: 1.0

TEOT: 0.005×237.52= 1.1876 g

EtOH= 0.15×46= 6.9 g

HCl = 0.01×36.5 = 0.365 g(100%)

\[
\frac{0.365}{0.374} = 0.9759 \text{ g; } 0.9759-0.365 =0.6109 \text{ g (water)}
\]

Water 0.07×18 = 1.26 g; 1.26-0.6109 = 0.6491 g

TEOTwt% = 12.23%, EtOHwt%= 71.04%, waterwt%12.97%, HCl wt%= 3.76%.

Calculate the recipe of sol of TIPP

Mole ratio: TIPP:water: EtOH: HCl = 0.5: 7: 15: 1.0

TIPP: 0.005×284.25 = 1.42125 g; 1.42125/97% = 1.4652 g
EtOH: \(0.15 \times 46 = 6.9\) g, HCl: \(0.01 \times 36.5 = 0.365\) g

\(0.365/0.374 = 0.9759\) g (water = \(0.9759 - 0.365 = 0.6109\) g)

Water: \(0.07 \times 18 = 1.26\) g; \(1.26 - 0.6109 = 0.6491\) g

TIPP wt\% = 14.22\%, EtOH wt\% = 69.07\%, HCl wt\% = 3.65\%, water wt\% = 12.61\%.

TIPP mol\% = 2.13\%, EtOH mol\% = 63.83\%, HCl mol\% = 4.25\%, water mol\% = 29.78\%.
REFERENCES


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I would also like to thank my friends and family for the support.