Use of Colloidal Crystal Templating to Fabricate Ordered Pit Arrays on Aluminum and Aluminum Alloy 3003

Newira Widharta
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Use of colloidal crystal templating to fabricate ordered pit arrays on aluminum and aluminum alloy 3003

by

Newira Widharta

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

MASTER OF SCIENCE

Major: Chemical Engineering

Program of Study Committee:
Kurt R. Hebert, Major Professor
Jennifer O’Donnell
Zhiqun Lin

Iowa State University
Ames, Iowa

2011

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# TABLE OF CONTENTS

| List of Figures | iv |
| List of Tables | viii |

1. Chapter 1: Introduction  
2. Chapter 2: Literature Review  
   2.1. Topographically Structured Etched Patterns on Metal Surfaces  
      2.1.1. Current Etching Processes for Lithography  
      2.1.2. Anodic Etching Using Mask  
      2.1.3. Colloidal Crystal Templating Method  
   2.2. General Anodizing Behavior on Aluminum and Aluminum Alloy 3003  
3. Chapter 3: Experimental  
   3.1. Sample Preparation  
   3.2. Polystyrene Suspension  
   3.3. Anodizing and Subsequent Processes  
   3.4. Scanning Electron Microscopy  
4. Chapter 4: Results and Discussion  
   4.1. Sample Characterization
4.2. Caustic Etching 23

4.3. Surface Preparation for Polystyrene Deposition 26

4.4. Polystyrene Deposition 28
  4.4.1. Effect of Solvent 28
  4.4.2. Effect of Polystyrene Concentration 33
  4.4.3. Effect of Polystyrene Functionalization 36
  4.4.4. Effect of Baking 37
  4.4.5. Effect of Polystyrene Particle size 40

4.5. Barrier Oxide Formation 42

4.6. Porous Oxide Formation 51

4.7. Pit Arrays Formed by the Polystyrene Template Process 53
  4.7.1. Aluminum Alloy 3003 Samples 53
  4.7.2. Aluminum Samples 57

5. Chapter 5: Conclusion 60

6. Chapter 6: References 63
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Aluminum electrograining sample</td>
<td>5</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Aluminum alloy 3003 surface after caustic etch dissolution</td>
<td>6</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Pit morphology from anisotropic anodic etching utilizing PDMS stamps</td>
<td>9</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Diagram of process for formation of tunnel pit array on Al utilizing inkjet printing</td>
<td>10</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>Resulting pit morphology by the method of inkjet printing</td>
<td>11</td>
</tr>
<tr>
<td>Figure 2.6</td>
<td>Diagram of oxide layer build-up around the polystyrene spheres utilizing constant current anodizing</td>
<td>13</td>
</tr>
<tr>
<td>Figure 2.7</td>
<td>Schematic diagram of fabrication of microporous alumina using polystyrene mask as template</td>
<td>14</td>
</tr>
<tr>
<td>Figure 2.8</td>
<td>Potentiodynamic response of AA2024</td>
<td>16</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>SEM of unetched aluminum alloy 3003 sample after mechanical polishing</td>
<td>21</td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>SEM of aluminum alloy 3003 after mechanical polishing and open circuit dissolution in 1M NaOH for 10 minutes</td>
<td>24</td>
</tr>
<tr>
<td>Figure 4.3</td>
<td>SEM of aluminum alloy 3003 after mechanical polishing and open circuit dissolution in 1M NaOH for 2 hours</td>
<td></td>
</tr>
<tr>
<td>Figure 4.4</td>
<td>SEM of as received aluminum alloy 3003</td>
<td></td>
</tr>
<tr>
<td>Figure 4.5</td>
<td>SEM of aluminum alloy 3003 electropolished for 7 minutes</td>
<td></td>
</tr>
<tr>
<td>Figure 4.6</td>
<td>SEM of aluminum after electropolishing for 5 minutes</td>
<td></td>
</tr>
<tr>
<td>Figure 4.7</td>
<td>SEM of 3 µm polystyrene spheres deposited on Al from water suspension (hydroxylated polystyrene spheres, concentration 2.0% w/v)</td>
<td></td>
</tr>
<tr>
<td>Figure 4.8</td>
<td>SEM of 3 µm polystyrene spheres deposited on Al from water suspension (hydroxylated polystyrene spheres, concentration 2.0% w/v)</td>
<td></td>
</tr>
<tr>
<td>Figure 4.9</td>
<td>SEM of 3 µm polystyrene spheres deposited on Al from ethanol-water suspension (solvent composition 10% ethanol and 90% water, hydroxylated polystyrene spheres with concentration 2.0% w/v)</td>
<td></td>
</tr>
<tr>
<td>Figure 4.10</td>
<td>SEM of 3 µm polystyrene spheres deposited on Al from ethanol-water suspension (solvent composition 90% ethanol and 10% water, hydroxylated polystyrene spheres with concentration 2.0% w/v)</td>
<td></td>
</tr>
<tr>
<td>Figure 4.11</td>
<td>SEM of 3 µm polystyrene spheres deposited on Al from water suspension (hydroxylated polystyrene spheres, concentration 2.5% w/v)</td>
<td></td>
</tr>
<tr>
<td>Figure 4.12</td>
<td>SEM of 3 µm polystyrene spheres deposited on Al from water suspension (hydroxylated polystyrene spheres, concentration 0.2% w/v)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.13  SEM of 3 µm nonfunctionalized polystyrene spheres deposited on Al from water suspension (concentration 0.2% w/v)

Figure 4.14  SEM of 3 µm hydroxylated polystyrene spheres deposited on Al, and baked at 110°C for 1 hour (concentration 2.0% w/v, solvent ethanol content 10%)

Figure 4.15  SEM of 3 µm hydroxylated polystyrene spheres deposited on Al, and baked at 130°C for 1 hour (concentration 2.0% w/v, solvent ethanol content 10%)

Figure 4.16  SEM of 3 µm hydroxylated polystyrene spheres deposited on Al, and baked at 150°C for 1 hour (concentration 2.0% w/v, solvent ethanol content 10%)

Figure 4.17  SEM of 3 µm hydroxylated polystyrene spheres deposited on Al, and baked at 110°C for 1 hour (concentration 2.0% w/v, solvent ethanol content 10%)

Figure 4.18  SEM of 10 µm carboxylated polystyrene spheres deposited on Al, and baked at 130°C for 1 hour (concentration 2.0% w/v, solvent ethanol content 30%)

Figure 4.19  Potential transients during anodizing of aluminum and aluminum alloy at 1mA/cm², with and without polystyrene spheres

Figure 4.20  Potential transients during anodizing of Al at 1mA/cm², for samples with monolayer and multilayer polystyrene coverage
Figure 4.21 Potential transients during anodizing of Al at 1mA/cm$^2$, showing effect of baking temperature on samples covered by monolayers of 3 µm hydroxylated polystyrene spheres

Figure 4.22 Potential-time curves during anodizing of Al at 1mA/cm$^2$ showing the effect of baking with no polystyrene spheres

Figure 4.23 Current transient during constant potential anodizing of aluminum (solid red line) and aluminum alloy (dashed blue line) at 20V, in 1M sulfuric acid

Figure 4.24 Low magnification SEM of aluminum alloy 3003 surface

Figure 4.25 Higher magnification SEM of aluminum alloy 3003 surface

Figure 4.26 SEM of Al with pit array formed by templating 3 µm hydroxylated polystyrene spheres

Figure 4.27 SEM of Al with pit array formed by templating 10 µm carboxylated polystyrene spheres
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Chemical composition (wt. %) of 3003 aluminum alloy samples</td>
<td>22</td>
</tr>
<tr>
<td>4.2</td>
<td>EDS composition measurements (wt.% at the marked points in Figure 4.1</td>
<td>22</td>
</tr>
</tbody>
</table>
In a number of industrial processes, metal surfaces are etched to develop topographic patterns consisting of microscopic cavities. Examples include aluminum electrolytic capacitors and lithographic printing. Al electrodes for electrolytic capacitors are etched to form a high density of pits, increasing the Al surface area to enhance capacitance. Al alloy plates for lithographic printing are etched to create a microscopically roughened surface that optimizes retention of ink and release agent. In each case, improvements can be made by increasing the ordering of the microscopic cavity arrangement. For capacitors, uniform pit spacing would allow the dielectric thickness (and thus the capacitor voltage) to be maximized for a given capacitance. In lithographic technology, the ordered microscopic structure could result in better control of retention of ink or release agent. This work focuses on the formation of ordered arrays of cavities on Al and Al alloy surfaces, for potential lithographic applications. The desired cavity depth and spacing are on the order of 1-10 micron.

In recent years, nanotechnology research has identified several techniques which could be deployed to produce ordered arrangements of nanoscale objects. It is possible that some techniques are adaptable to the micron-scale topography appropriate for lithographic technology. Chapter 2 discusses the different techniques that had been developed previously and explains why colloidal crystal templating method is suitable for this application. We choose such a technique, previously developed for aluminum electrolytic capacitors, and adapt it to aluminum alloy 3003 substrates used in the solid-ink lithography. We show that ordered pit arrays with size and spacing of 1 µm to 10 µm can be obtained. The length scale
of the pit size and spacing is the same as that of disordered pit patterns obtained by current etching processes, but the pit ordering is dramatically increased.
Chapter 2: Literature Review

2.1 Topographically Structured Etched Patterns on Metal Surfaces

Traditional liquid ink lithographic printing involves establishing image (printed) and non-image (not printed) areas, based on selective application of ink (1). Hydrophilic and oleophilic surfaces provide this selectivity. The non-image areas are generally hydrophilic and image areas oleophilic, thus, the oil based inks are repelled from the non-image areas after water has been applied to the substrate. In photolithography, image and non-image areas can be produced by processes which include a step of exposing a layer of image material on the surface to radiation. The radiation exposure creates solubility differences in the image material corresponding to printing and non-printing area.

The concept of solid ink based print process differs from the liquid ink based printing, in that the ink is solid at normal ambient temperatures. In the ink-jet printing device, the ink is melted into liquid that is jetted to produce image. The image is deposited on an imaging drum which has been coated with a release agent.

In many lithography processes, aluminum substrates are used as lithographic plates. General roughening of the surface is mandatory in order to improve the adhesion of the subsequently applied light-sensitive coating, release agent, and also to improve the water retention in the non-image areas during printing (2). Surface roughening is generally obtained by caustic etching or electrograining processes that produce a large number density of corrosion pits.
The pit size and number density affect the efficiency of the process and the image quality. For example, surface roughening has a large influence on the transfix efficiency and the quality of the image, since more ordered pits tend to spread the release agent more evenly on the paper. In addition, the pit size impacts the amount of release agent that is retained after each print in the solid-ink process; this in turn affects consumable life, as well as producing secondary impacts of release agent being carried through the paper path. Typical pit sizes produced during successful etching process range from 8 – 20 µm, with these pits covered approximately about 40-50% of the total surface area. It is possible that controlled pit sizes in an ordered spacing can increase the efficiency of the solid ink lithography.

Several methods of producing this special ordered topography are available. In the following section, existing etching processes for lithography are reviewed. Typically, electrograining is used for liquid ink lithography and caustic etching for the solid ink process. Each process has special characteristics in regards of the micro/nano structure produced and will be described briefly.

2.1.1 Current Etching Processes for Lithography

In the electrograining process, the surface of the lithographic plate (e.g. aluminium) is uniformly roughened (1). Uniformly pitted and convoluted surfaces are developed through a controlled corrosion process, which improves the retention of water and image material. The resultant morphology, the pit formation process, and the etch film produced as a corrosion product have been studied extensively (3-13).
Generally, electrograining is applied by alternating cathodic and anodic voltage or current on Al electrodes, utilizing a suitable electrolyte (14). During the positive half period of the ac cycle, aluminum is dissolved from the surface by the formation of Al$^{3+}$ ions. During the negative half period, the etch film is formed and deposited on the aluminum surface by a pH-controlled dissolution-precipitation mechanism (5,6,12).

![Aluminum electrograining sample](image)

**Figure 2.1.** Aluminum electrograining sample (15).

Typically, electrograining forms large hemispherical pits, each of which is composed of a large number of fine cubic pits (Figure 2.1) (15). Electrolyte composition and surface condition play important roles in determining the pit morphology. Also, the amount of charge passed through the electrode affects the final morphology of the electrograined surface, and increasing the current density leads to a coarser topography. Moreover, electrolyte temperature and the frequency also strongly influence the surface morphology (7,
Several electrolytes (nitric acid and hydrochloric acid) produce different type of pits. Nitric acid generally produces a “pits-within-a-pit” structure with shallow depth, which is useful for delicate printing. Hydrochloric acid, on the other hand, produces finer pits which are suitable for other printing purposes (2).

Caustic etching is used for the preparation of the lithographic plates used for solid ink-based process. During caustic etching, surface dissolution is observed, both in aluminum (16-17) and aluminum alloy 3003 (2). However, the pits produced on aluminum alloy 3003 are much larger compared to the pure aluminum counterpart, which might be the effect of the inter-metallic phases present on the alloy surface.

Figure 2.2. Aluminum alloy 3003 surface after caustic etch dissolution.
From Figure 2.2, it can be seen that the pits' average size is 10 µm. The mechanism of how these pits develop on either aluminum or alloy 3003 is not yet known. For aluminum, it is known that several factors influence the development of pits during dissolution, such as the surface pretreatment before anodic etching (17), and also the thermal and mechanical processing of the foil (16).

The discussion above demonstrates the usefulness of electrograining and caustic etching in preparing lithographic surfaces by surface roughening; however, there are several downsides to these processes. For example, electrograining requires a significant amount of electrical energy. Moreover, while these processes roughen the surface, it is hard to produce a consistent and ordered topographic structure, as the size and spacing of pits cannot be controlled. Thus, these processes can be improved by the use of templates allowing the spacing and pit size to be consistently controlled.

### 2.1.2 Anodic Etching Using Masks

Formation of topographically ordered etched microstructures has been investigated for applications to aluminum electrolytic capacitors. High-voltage capacitors are typically produced by dc etching of Al foils (18-20). For high-power capacitors, it is important to maximize the surface area of the electrode, because the surface area determines the capacitance. Anodic "tunnel etching" of (100) oriented Al foil in HCl electrolyte is widely used for the enlargement of surface area (21-35). Tunnel etching results in the formation of tunnel-shaped micron-wide pits by selective dissolution of the (100) face. For applications to
high-voltage electrolytic capacitors, a spacing between adjacent pits of several microns is required, given the thickness of the oxide film used as dielectric. Dispersion of initiation sites of pits has been improved by changing the chemical composition of the substrate (36-37). However, the tunnel depth and thus the surface area may be limited by undesirable lateral dissolution of Al, which tends to merge pits (38) Therefore, improvements in pit distribution density and homogeneity of pit sizes, while avoiding an excessive dissolution of the aluminum surface, can further increase the surface area of etched aluminum capacitor electrodes (39).

Various mask techniques have been investigated to form ordered etch patterns for electrolytic capacitor applications. It is possible that similar techniques could be applied to control pit sites for lithographic applications, if different etching processes are used to produce rounded rather than tunnel-shaped pits.

*Anisotropic Anodic Etching utilizing PDMS stamps*

Utilizing anisotropic anodic etching and PDMS (polydimethylsiloxane) stamps, trench and pit microstructure have been produced on aluminum surfaces (40, 41). By applying these stamps, a thin polymer mask with periodic line and space pattern is obtained, that enables selective anodic etching to produce the trench structure. The shape and the depth of the trench structure is sensitive to temperature.

Pit structures were also produced with PDMS stamps (Figure 2.3). Reducing the applied current density at an appropriate rate (200 mA/cm²’s) was effective for the suppression of the
undesirable lateral dissolution of Al. Moreover, the addition of small amount of H$_2$SO$_4$ to HCl electrolyte increased the depth of the obtained tunnel pits. With these factors, tunnel pits with depth over 50 µm could be produced. (40)

Figure 2.3. Pit morphology from anisotropic anodic etching utilizing PDMS stamps. (40)
**Inkjet Printing**

Etching microstructures on Al may also be produced using masks deposited by inkjet printing (42). Inkjet printing can make desirable patterns on a substrate in noncontact mode.

![Diagram](image)

Figure 2.4. Diagram of process for formation of tunnel pit array on Al utilizing inkjet printing: (a) high resolution inkjet printing of acrylic resin on Al foil, (b) dot array of acrylic resin on Al, (c) formation of oxide layer by anodizing, (d) removal of acrylic resin, and (e) anodic etching of Al in HCl solution (43).

As shown in Figure 2.4, a dot array of polymer resin was formed on Al (100) and was transferred to the oxide layer by anodizing. The anodic etching of Al with a mask in a HCl
electrolyte resulted in the site-controlled initiation of etch tunnels, producing uniform pits with high aspect ratio. The interval of the tunnel pits could be controlled at the micrometer scale (43). Recent research has demonstrated ability in patterning high resolution (~3um) intervals of dot arrays (44).

Figure 2.5. Resulting pit morphology by the method of inkjet printing (43)
2.1.3 Colloidal Crystal Templating Methods

Masks based on colloidal spheres have been used by Ono’s group, to improve the ordering of pits for capacitor etching. A two-dimensional array of colloidal polystyrene spheres was prepared by self-assembly on an aluminum substrate (45-46).

The stable close-packed (cp) pattern was due to particle interactions between the spheres. It was considered that neither electrostatic repulsion nor Van der Waals attraction forces between spheres controlled cp structure formation. Instead, the main factors governing the stable array were thought to be the attractive capillary forces (due to the menisci formed around the particles) and the convective transport of particles toward the ordered region (45-46). Another controlling factor for the 2D array was the suspension evaporation rate (45).

The transfer of the hexagonally ordered pattern of self-assembled colloidal spheres to the aluminum substrate could be achieved by anodic oxide growth, followed by selective etching of the exposed aluminum surface (47). Anodizing was carried out in two steps. In the first step in neutral solution, the growth of a barrier-type film was partially suppressed in the contact area between the spheres and the underlying aluminum substrate, resulting in the formation of ordered dimple arrays in an anodic oxide film (48) (Figure 2.6). Steps c - f in Fig. 2.7 describe the formation of ordered pits using the anodic barrier oxide mask.
Figure 2.6: Diagram of oxide layer build-up around the polystyrene spheres utilizing constant current anodizing. (shaded area in gray). The ratio of oxide thickness to particle diameter is exaggerated for clarity.

After the first anodizing step, the polymer spheres are removed by dissolution in an organic solvent (step (c)). Then, in the second anodizing step, a porous oxide layer is grown at the original polystyrene contact area (d). As the applied potential is lower than that during the first anodizing step, the porous oxide is formed only at these sites, and the barrier film does not grow. Porous oxide formation produces a controlled enlargement of the unmasked areas. The process includes the removal of the nanoporous region by chemical etching using the difference in structural dimensions between the porous regions and the barrier oxide remains surrounding the polystyrene sites (48). Finally, tunnel pits are formed by DC etching on the unmasked metal (f).
Figure 2.7. Schematic diagram of fabrication of microporous alumina using polystyrene mask as template; (a) self assembly polystyrene spheres, (b) first anodizing in neutral solution, (c) removal of spheres, (d) second anodizing in acid solution, (e) removal of nanoporous layer, and (f) and (g) electrochemical etching of aluminium with a patterned alumina mask. (49)
2.2 General Anodizing Behavior on Aluminum and Aluminum Alloy 3003

The colloidal mask technique is appropriate for lithographic applications because the size and spacing of the mask features is compatible with that required by lithography. However, the technique has not previously been applied to aluminum alloys used for lithographic substrates. It is not presently known whether suitable barrier and porous oxide films can be grown on these alloys. Formation of the barrier oxide layer on the surface of aluminum and aluminum alloy is critical for the colloidal mask process. Therefore the basic principles of oxide film growth on Al and Al alloys are discussed briefly here.

The anodic reaction that occurs during anodizing is

\[ 2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \]

The ionic current through the anodic film is very sensitive to the electric field in the film. Therefore, the oxide layer forms uniformly according to a thickness-voltage ratio of approximately 1.3 nm/V. This ratio is referred to as the "anodizing ratio."

As an example of anodizing on aluminum alloys, film growth on aluminum alloy 2024 has been studied for both neutral and acidic electrolytes. Even with the presence of intermetallic particles on the alloy, anodic films are produced, but with reduced efficiency compared to Al.

Potentiodynamic film growth is illustrated in Fig. 2.8. Potentiodynamic curves displayed two peaks which can be associated with the oxidation of Al-Mg-Cu and Al-Cu-(Fe) containing second phase. This potentiodynamic experiment suggests that intermetallic particles may not interfere with anodizing. It remains to be seen whether this is true for the aluminum alloy 3003 which is the basis for the present work.
Figure 2.8. Potentiodynamic response of AA2024. The two peaks correspond to the oxidation of Al-Mg-Cu and Al-Cu-(Fe) second phase particles. (50-51)
Chapter 3: Experimental

This chapter describes general experimental procedures used to produce pit arrays on aluminum and aluminum alloy 3003 surfaces. Further details of optimized procedures, developed in the course of the work, are described in Chapter 4.

3.1 Sample Preparation

Both aluminum and aluminum alloy 3003 samples were used in the experiments. Al specimens were 99.99% purity, 110 µm thick foils (Toyo Corp.). These foils were provided in the as-annealed condition and had a typical grain size of 100 µm, as a result of the extended duration of the final annealing step. Alloy 3003 foil samples were AA3003 H-14 (Advanced Materials) with reported composition 96.7% Al, 0.050% Cu, 0.70% Fe, 1.0% Mn, 0.60% Si, and 0.10% Zn. The thickness of the alloy foils was 0.05 mm.

Flat surfaces for both materials (Al and AA3003) were critical for successful deposition of ordered polymer spheres. To achieve this, samples were electropolished or mechanically polished. Electropolishing was carried out in a solution containing 20% perchloric acid and 80% ethanol (v/v). A constant potential of 30V was applied between the aluminum foil and a platinum counter electrode for extended times with electropolishing solution temperature maintained at 5°C. A constant voltage DC power supply (BK Precision) was used to apply the specified potential. The exposed electrode area during the process was 5cm². A platinum counter electrode was attached in a semicircular shape over aluminum foil in order to provide
a uniform potential distribution over the electrode surface. For aluminum 5 minutes of electropolishing were sufficient, whereas a longer time of 7 minutes was required to achieve relatively flat surface in the AA3003 samples.

Mechanical polishing was also investigated as a means to flatten the alloy surfaces. The samples were polished using a series of papers from 200, 400, 800, to 1200 grit. Alloy samples were typically held down with surfaces exposed to the rotating abrasive paper, while being washed with water and ethanol. The final step used a diamond coating suspension in order to give a reflecting finish to the surface of the 3003 alloy. In our experiments, the electropolishing process was more convenient than mechanical polishing, because of the smaller time needed to produced the required surface finish.

### 3.2 Polystyrene Suspension

Polystyrene spheres of different sizes and surface functionalization (3 \( \mu m \) polystyrene, 3 \( \mu m \) hydroxylated polystyrene, and 10 \( \mu m \) carboxylated polystyrene) were obtained from Polysciences. The spheres were supplied as suspensions in water with concentration of 2.5% solids (w/v) and diameter variance 5%. As-received aqueous polystyrene suspensions were diluted with water-ethanol mixtures to the desired final concentrations (see Chapter 4).

A drop of the suspension was placed on the sample surface with volume 25 \( \mu l \) for aluminum and 40 \( \mu l \) for aluminum alloy samples. The drop was allowed to dry in open air (22°C) for 1 day in order for the spheres to self-assemble into a closely packed structure via attractive capillary forces. After the spheres self-assembled, the samples were then heated in a
laboratory oven (Fisher Scientific Isotemp) for 1 hour at a temperature higher than the glass transition point of the polystyrene (93°C) in order to fix the spheres into the sample surface by sufficiently melting the polystyrene.

3.3 Anodizing and Subsequent Processes

For the following anodizing processes, two solutions were needed; 0.5M boric acid-0.05M sodium tetraborate for the first barrier oxide anodizing step, and 1M sulfuric acid for the second porous oxide formation step. All solutions were made from reagent grade chemicals and nanopure water.

During the anodizing processes, the circular working electrode area of 1.767 cm² was exposed to the solution, which had been covered with polystyrene deposit. A low-current power supply (Keithley 2400A) was used for both anodizing processes. Full coverage of the anodized surface with polystyrene spheres was necessary for successful fabrication of pit arrays.

The purpose of the first anodizing step was to create a barrier oxide film between the assembled polystyrene spheres. This process was carried out using constant current density (1mA/cm²) until a potential of 25V was attained. The samples were then rinsed in deionized water for 1 minute to clear the residue. After the film was created, the next step was to remove the polystyrene spheres from the surface utilizing toluene. Samples were immersed in toluene for 5 minutes to ensure that all spheres are dissolved, and then rinsed in the deionized water again. Depending on the amount of the polystyrene layer, the immersion
could be extended. The second anodizing step then followed after the removal of the spheres. This anodizing procedure was conducted at a constant potential, lower than the value of 25 V obtained during barrier oxide formation. Because of the reduced potential, a porous oxide film was formed only on the area not covered by the barrier layer. If the second anodizing potential was larger than that of the first anodizing, porous oxide would have been formed uniformly on the entire sample surface. The extent of metal consumption during porous oxide formation determined the depth of the final pits. The second anodizing step was performed at 20V for 5 minutes in 1M sulfuric acid solution.

Finally, both the barrier oxide mask and the porous oxide in the pits were removed. Two solutions were used in this step: 5 wt. % phosphoric acid at 30°C for 60 minutes, or 5 wt. % chromic acid and 20 wt. % phosphoric acid at 70°C for 3 minutes. The chromic acid solution was used in most cases because it eliminates metal dissolution in during oxide removal, as a passivating chromium oxide film is formed on the metal once oxide dissolution is complete.

3.4 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM, Hitachi S-2460N) was the main tool used in imaging the samples. Samples were cut (1x1 cm) and covered in sputtered gold layers in order to produce conductive surfaces suitable for SEM imaging. Energy Dispersive Spectroscopy (EDS) was also used for characterizing the chemical content of the samples and the second phase particles.
Chapter 4: Results and Discussion

4.1 Sample Characterization

The intermetallic phases in aluminum alloy 3003 samples were characterized because of the possible influence of these phases on subsequent anodizing steps.

Figure 4.1. SEM of unetched aluminum alloy 3003 sample after mechanical polishing.

Numbers mark composition measurements in Table 4.2
Commercially available aluminum alloy 3003 samples from different sources typically vary in the content of alloying elements (Si, Mn, Fe, and Cu). Composition of aluminum alloy specimens are shown in Table 4.1. Spatially averaged EDS measurements of the samples used in this work are compared with the reported composition of AA3003 from a different source (52). The relative enrichment of alloying elements in the present samples may be due to selective Al dissolution during etching.

Table 4.1: Chemical composition (wt.%) of 3003 aluminum alloy samples

<table>
<thead>
<tr>
<th>Material</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Al</th>
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<tbody>
<tr>
<td>Davodi, et al (EN AW-3003)</td>
<td>0.15</td>
<td>0.48</td>
<td>0.12</td>
<td>1.1</td>
<td>0.03</td>
<td>98.12</td>
</tr>
<tr>
<td>Present work (after etching)</td>
<td>0.28</td>
<td>0.645</td>
<td>0.204</td>
<td>2.961</td>
<td>0.536</td>
<td>87.608</td>
</tr>
</tbody>
</table>

Table 4.2: EDS composition measurements (wt.%) at the marked points in Figure 4.1

<table>
<thead>
<tr>
<th>Point #</th>
<th>Al</th>
<th>Si</th>
<th>Mn</th>
<th>Mg</th>
<th>Fe</th>
<th>Cu</th>
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<td>1</td>
<td>51.527</td>
<td>0.115</td>
<td>29.188</td>
<td>0.126</td>
<td>18.091</td>
<td>0.954</td>
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<td>0.048</td>
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<td>1.107</td>
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<td>3.455</td>
<td>0.199</td>
<td>1.285</td>
<td>1.57</td>
</tr>
</tbody>
</table>
EDS composition measurements at the selected points in Figure 4.1 are presented on Table 4.2. Points 1-2 and 4 correspond to intermetallic particles and point 3 to the alloy matrix. The results can be compared to common inter-metallic particles in aluminum alloys. Point 1 was rich in Mn and Fe particles, and it could possibly correspond to Al$_6$(Mn,Fe) phase. Point 2 was rich in Si. Since no reports of intermetallic AlSi phases highly enriched in Si were found, this phase may be pure Si (53). The shape of these two types of particles differed; the particles rich with Mn resembled long blocks, whereas particles rich in silicon had irregular shapes. Point 3 were the matrix of the 3003 alloy as it was very rich in the aluminum content with around 2-3% Mn. The composition of point 4 is similar to the matrix of the 3003 alloy as it was also very rich in aluminum content, however the alloying elements are apparently enriched relative to the matrix; this intermetallic phase may be Al$_{12}$(Mn, Fe)$_3$Si. The samples of the Davodi, et al mainly showed the Al$_6$(Mn,Fe) and Al$_{12}$(Mn, Fe)$_3$Si phases, both with Mn/Fe ratio of 1:1. In contrast to the alloy, aluminum samples showed no indication of second phase particles, due to their high purity.

4.2 Caustic Etching

Controlled surface topography on aluminum alloy lithographic plates is presently achieved by etching processes. Samples of caustic etched samples are presented here for comparison to those result presented later using the polystyrene templating method.

Figure 4.2-4.3 show AA3003 surfaces after caustic etching for different times. Figure 4.2 shows the alloy after open circuit dissolution for 10 minutes, whereas the sample in Figure
4.3 was dissolved for 2 hours. All samples in the figures were mechanically polished prior to etching, using the methods described in the Experimental chapter. The pit size depended significantly on time, longer etching times producing larger pits. In the 10 minute experiment, the pit size was roughly 9 µm, whereas after 2 hours, the size almost tripled to about 25 µm. Figures 4.2 and 4.3 also reveal considerable variability of pit size and depth on a given surface.

Figure 4.2. SEM of aluminum alloy 3003 after mechanical polishing and open circuit dissolution in 1M NaOH for 10 minutes.
Figure 4.3. SEM of aluminum alloy 3003 after mechanical polishing and open circuit dissolution in 1M NaOH for 2 hours.
4.3 Surface Preparation for Polystyrene Deposition

SEM images of received aluminum and electropolished alloy 3003 samples are presented in Figures 4.4 and 4.5. Electropolishing effectively removed ridges on the as-received sample due to rolling. The small pits in Fig. 4.5 correspond to the size and shape of intermetallic particles. Apparently, intermetallic particles are preferentially dissolved or eroded by the electropolishing process.
In contrast, electropolished aluminum samples appear completely flat in SEM (Figure 4.6). The only topographic difference between electropolished Al and AA 3003 were the pits left by intermetallic particles in the alloy. However, the objectives of the electropolishing process to remove ridges and flatten the surface were attained. Surface flatness is important for successful deposition of polystyrene sphere arrays.

Figure 4.5. SEM of aluminum alloy 3003 electropolished for 7 minutes.
4.4 Polystyrene Deposition

4.4.1 Effect of Solvent

The addition of ethanol to the initially aqueous polystyrene particle suspension was explored to enhance the spreading of the suspension across the surface of the sample. It was necessary to achieve complete monolayer coverage of polystyrene spheres for successful mask formation by anodizing. Although localized monolayer coverage could be achieved without the addition of ethanol, the downside was a small coverage area. With the addition of small amount of ethanol, larger droplet surface area could be achieved due to the reduced surface
tension of the liquid/air interface. In addition, to precondition the aluminum and the 3003 alloy surfaces, the samples were immersed in the water-ethanol solution and let dry in the open air before the drop of suspension was added to the sample.

Figure 4.7. SEM of 3 μm polystyrene spheres deposited on Al from water suspension (hydroxylated polystyrene spheres, concentration 2.0% w/v).
Figure 4.8: SEM of 3 µm polystyrene spheres deposited on Al from water suspension (hydroxylated polystyrene spheres, concentration 2.0% w/v). Magnified view showing edge of polystyrene deposit.

Figures 4.7 and 4.8 show SEM images of Al surfaces after deposition of polystyrene spheres from a water suspension. Without the addition of the ethanol, it was clear that multilayers of polystyrene sphere were formed on the surface of the samples. Simple visual inspection also indicated that the polystyrene drops were clumped together, not dispersing to the open area of the samples. This resulted in very small area of coverage (area ~0.5 cm²) compared to working electrode area (area = 1.767 cm²). After the drying process, it was also seen that the
dried area covered by the polystyrene contracted further, forming a very thick multilayer deposit.

Figure 4.9. SEM of 3 µm polystyrene spheres deposited on Al from ethanol-water suspension (solvent composition 10 % ethanol and 90% water, hydroxylated polystyrene spheres with concentration 2.0% w/v).

The effect of addition of ethanol to the suspension is seen in Figure 4.9. Unlike the sample in Figures 4.7 and 4.8, where a multilayer was clearly present, it is clear in Figure 4.9 that only a monolayer of polystyrene spheres was formed. Locally, clusters of polystyrene spheres
were arranged in hexagonal cp structures, even though the overall deposit was not as tightly packed as those formed from aqueous suspensions. The effect of ethanol is partly due to the increased dispersion of the droplet caused by lower surface tension. Also, faster drying would have resulted from the relatively high vapor pressure of ethanol, perhaps reducing the contraction of the drop during drying. However, as shown in Figure 4.10, too much ethanol content would produce excessive spreading of the monolayer, and a much lower coverage of the cp structure. Another effect would be the increase the evaporation rate of the solution, effectively drying the surface before the spheres had chance to assemble into an ordered arrangement. Thus, the ethanol content was optimized to maximize the area of coverage by the monolayer, while still maintaining the cp structure. Even at the optimum ethanol content, complete coverage by the ideal monolayer cp structure was not generally possible.
Figure 4.10. SEM of 3 µm polystyrene spheres deposited on Al from ethanol-water suspension (solvent composition 90 % ethanol and 10% water, hydroxylated polystyrene spheres with concentration 2.0% w/v).

4.4.2 Effect of Polystyrene Concentration

Commercially available polystyrene spheres, whether nonfunctionalized, hydroxylated or carboxylated, were typically available at a concentration of about 2.5% (w/v). While this concentration led to deposits with close packed structures, multilayers were usually present with small coverage area after the drying process. Comparison of Figures 4.11 and 4.12 with Figure 4.7 show the effect on the deposit structure of the polystyrene concentration in
aqueous suspension. The polystyrene suspension of Figure 4.11 was undiluted. It can be seen that this solution produced multilayer deposits with highly-ordered top layers.

Figure 4.11. SEM of 3 µm polystyrene spheres deposited on Al from water suspension (hydroxylated polystyrene spheres, concentration 2.5% w/v).
Figure 4.12. SEM of 3 µm polystyrene spheres deposited on Al from water suspension (hydroxylated polystyrene spheres, concentration 0.2% w/v).

At the low polystyrene concentration of 0.2% (w/v), Figure 4.12 shows that spheres did not form a cp structure because of the low density of spheres. In addition, the area of coverage was only improved slightly relative to Figure 4.7, probably because of the comparatively high surface tension of the aqueous droplet. However, both the polystyrene concentration and solvent concentration were varied in optimizing monolayer deposit coverage. The best combination was judged to be 2% w/v.
4.4.3 Effect of Polystyrene Functionalization

In the initial stage of the work, nonfunctionalized polystyrene spheres were used. However, poorly ordered polystyrene sphere deposition was obtained, due to the hydrophilic surface of the aluminum in contrast to the hydrophobic surfaces of the polystyrene spheres. Also, only a small fraction of the spheres were left attached after the first anodizing step, resulting in low density of openings available for pit formation.

Figure 4.13. SEM of 3 µm nonfunctionalized polystyrene spheres deposited on Al from water suspension (concentration 0.2% w/v).
Comparison of Figures 4.12 and 4.13 illustrates the effect of hydroxyl functionalization, since both suspensions contained the same polystyrene concentration. It is seen that the coverage of hydroxylated polystyrene spheres is much higher after drying.

### 4.4.4 Effect of baking

After polystyrene particles self-assembled into large monolayer area, baking was carried out to fix the particles in position on the surface of aluminum or 3003 alloy. Without the heating process, detachment of the spheres was observed during anodizing, possibly due to compressive stresses associated with oxide formation. Detachment was manifested by large voltage fluctuations and a reduction of the sphere coverage. Baking treatments were carried out above the glass transition temperature \( T_g \) of polystyrene, approximately 93 °C.

Figures 4.14-4.16 illustrate the effect of baking temperature for 3 µm hydroxylated spheres. The best temperature was near 110°C (Figure 4.14), since the shape and position of the spheres were preserved. Higher baking temperatures, as shown in Figures 4.15 and 4.16, resulted in melting of the spheres and appreciable merging of particles by flow. It is noted that different optimum baking conditions (130°C for 1 hour) were found for 10 µm polystyrene carboxylate spheres, because of either differences of particle size, end group, or crosslink density and molecular weight. For the optimum baking treatment, the polystyrene spheres were melted just enough for it to be fixed to the underlying sample surface.
Figure 4.14. SEM of 3 µm hydroxylated polystyrene spheres deposited on Al, and baked at 110°C for 1 hour (concentration 2.0% w/v, solvent ethanol content 10%).
Figure 4.15: SEM of 3 µm hydroxylated polystyrene spheres deposited on Al, and baked at 130°C for 1 hour (concentration 2.0% w/v, solvent ethanol content 10%).
Figure 4.16. SEM of 3 μm hydroxylated polystyrene spheres deposited on Al, and baked at 150°C for 1 hour (concentration 2.0% w/v, solvent ethanol content 10%).

4.4.5 Effect of Polystyrene Particle Size

Pit spacings of around 10 μm are favored for applications such as lithographic plates. Since 10 μm hydroxylated polystyrene spheres were not available commercially, carboxyl functionalized 10 μm spheres, which were also hydrophilic, were used instead.
Figure 4.17. SEM of 3 µm hydroxylated polystyrene spheres deposited on Al, and baked at 110°C for 1 hour (concentration 2.0% w/v, solvent ethanol content 10%).

Figures 4.17 and 4.18 compare deposits after baking, formed from 3 µm hydroxylated spheres (Figure 4.17) and 10 µm carboxylated spheres (Figure 4.18). The 3 µm hydroxylated spheres did not form cp structures as effectively as did the 10 µm carboxylated spheres. It should be noted that the optimum ethanol content for the 3 µm spheres was smaller that that for the 10 µm spheres. The different size of the polystyrene spheres also affected the baking temperature of each experiment. Despite the higher baking temperature in Figure 4.18, the extent of merging of spheres due to flow of melted polystyrene was smaller than was the case for 3 µm spheres.
Figure 4.18. SEM of 10 µm carboxylated polystyrene spheres deposited on Al, and baked at 130°C for 1 hour (concentration 2.0% w/v, solvent ethanol content 30%).

4.5 Barrier Oxide Formation

The next step after polystyrene deposition was anodic oxide formation in neutral pH solution, in order to form a protective barrier layer on the portion of the surface not covered by polystyrene particles. The effects of several critical factors were observed, such as the influence of polystyrene during anodizing, and the effect of baking. These effects are inferred from plots of potential vs. time during anodizing, presented in this section.
On a flat surface with no polystyrene particles, barrier film growth in neutral solutions proceeds with high efficiency. Chemical or geometric effects of polystyrene spheres on anodizing could be inferred by comparison of voltage transients to the ideal case of film growth on open surfaces with 100% current efficiency.

\[
A \times \frac{dN_{Al_2O_3}}{dt} = A \times \frac{i}{6F} \tag{1}
\]

\[
\frac{dV}{dt} \times \frac{1}{\varepsilon_f} \times \frac{\rho_{Al_2O_3}}{M_{Al_2O_3}} = \frac{i}{6F} \tag{2}
\]

where \(i\) is the applied current density, \(F\) is Faraday's constant (96,484 C/mol), \(A\) is the electrode area (1.767 cm\(^2\)), and \(\varepsilon_f\) is the electric field in the oxide layer. From Equations 1 and 2, the ideal rate of the potential growth (dV/dt) at current densities used in this work is 0.08 V/s (for 0.1 mA/cm\(^2\)) or 0.8 V/s (for 1 mA/cm\(^2\)). These values represent the ideal rate where oxide layer grew on all of the open surface area, and where there were no polystyrene spheres present on the sample. Comparing the experimental and ideal rates of potential increase, the anodizing efficiency is deduced,

\[
\eta = \frac{(dV/dt)_{actual}}{(dV/dt)_{theoretical}} \times 100\% \tag{3}
\]

where dV/dt is the rate of potential increase, and \(\eta\) is the anodizing efficiency.
Figure 4.19. Potential transients during anodizing of aluminum and aluminum alloy at 1mA/cm$^2$, with and without polystyrene spheres. Results are shown for Al without polystyrene spheres (solid green line, 5 min electropolishing, slope 0.9 V/s); Al with carboxylated 10 µm polystyrene spheres (red dashed line, 5 min electropolishing, 1.85% (w/v) polystyrene in 30% ethanol, baked at 130°C for 1 hour, slope 0.7 V/s); AA 3003 without polystyrene spheres (purple dotted line, 7 min electropolishing, baked at 130°C for 1 hour, slope 0.75 V/s); AA 3003 with carboxylated 10 µm polystyrene spheres (blue diamonds, 7 minute electropolishing 1.85% (w/v) polystyrene in 30% ethanol, baked at 130°C for 1 hour, slope 0.5 V/s).
The anodizing behavior of aluminum and aluminum alloy, both with and without polystyrene spheres, is illustrated in Fig. 19. For the unbaked Al sample with no polystyrene, the initial potential was close to 0 V, whereas for the samples which had been heated, the potential jumped to 3-5 V upon applying the current. This means that thermal oxide growth occurred during the heating process, producing an initial oxide layer of several nm thicknesses.

After the initial potential jump, steady linear potential growth could be seen (slower for the samples with polystyrene spheres). The experimental slope for the Al sample with no polystyrene was 0.9 V/s, close to the calculated slope of 0.8 V/s for 100% current efficiency. The slope on the Al sample with polystyrene spheres was reduced from this value, 0.7 V/s. Based on the masking effect of the spheres, a higher slope would have been expected, since masking would increase the true current density. This effect may be insignificant if the contact area is small between the sphere and substrate. In any case, the reduced potential slope on the polystyrene-covered sample suggests that the anodizing current efficiency was smaller due to polystyrene. The chemical mechanism of this effect is not clear, but decreases of anodizing current efficiency can frequently be attributed to oxygen evolution as a side reaction. The figure also indicates that polystyrene reduced the anodizing current efficiency on the alloy as well as on Al.

Finally, Figure 4.19, also illustrates the slower potential increases typically found on alloy samples prepared using similar procedures. The apparently reduced current efficiency of the alloy is probably due to oxygen evolution on remnants of intermetallic particles left after electropolishing.
Figure 4.20. Potential transients during anodizing of Al at 1mA/cm², for samples with monolayer and multilayer polystyrene coverage. Al with monolayer of 3 μm hydroxylated polystyrene spheres (dotted blue line, 5 minutes electropolishing, 2% w/v polystyrene in 10% ethanol, baked at 115°C for 1 hour, slope 0.5 V/s). Al with multilayer coverage of 3 μm hydroxylated polystyrene spheres (red line, 5 minutes electropolishing, 2.5% w/v polystyrene in water, baked at 115°C for 1 hour, 0.07 V/s).

Figure 4.20 shows potential transients during anodizing of Al surfaces with either monolayer or multilayer sphere coverage. The dotted blue line represented the samples with
approximately full area of coverage of single layer of polystyrene spheres with cp structure, while the red line represented the samples with multilayer area of coverage of spheres. The sample with full coverage of polystyrene spheres yielded a higher slope compared to the sample with the multilayer. The slope (dV/dt) of full area coverage was around ~0.5 V/s while for the multilayer sample, the slope was around ~0.07 V/s which was almost slower by an order of magnitude. Again, these results did not conform to the expectation based on the open area for anodizing. During the anodizing process, with the polystyrene spheres attached, there was apparently a side process, besides the forming of oxide layer, that reduces the current efficiency of anodizing process.
Figure 4.21. Potential transients during anodizing of Al at 1mA/cm², showing effect of baking temperature on samples covered by monolayers of 3 μm hydroxylated polystyrene spheres. In both experiments, deposition was from 2% w/v polystyrene suspension in 10% ethanol, and baking was carried out for 1 hour after 1 day drying. Solid blue line, Baking temperature 110°C (solid blue line), 130°C (dashed green line), 150°C (dotted red line).

Figure 4.21 shows the effect of baking temperature on potential-time plots, for samples with polystyrene monolayer deposits. Baking of these samples were performed for one hour with different temperatures at 110°C, 130°C, and 150°C, represented by the solid blue line, dashed
green line, and dotted red line respectively. Higher baking temperatures resulted in larger rates of potential increase, indicating smaller anodized area or larger current efficiency. However, the former possibility is unlikely since Figures 4.14 – 4.17 suggest that the open area decreases due to melting. The effect of the baking temperature on aluminum surfaces without polystyrene spheres is shown in Figure 4.22. In this figure, the samples were dipped in the 28% ethanol-water solution and then baked at the specified temperature. Anodizing at constant current density (1 mA/cm²) was then performed. Regular anodizing behavior was found after the initial potential jump. The slope of the graph was close to 0.8 V/s for all curves, indicating high current efficiency. Therefore, the effect of baking temperature in Figure 4.22 must be due to the effect of polystyrene on the anodizing current efficiency.
Figure 4.22. Potential-time curves during anodizing of Al at 1mA/cm² showing the effect of baking with no polystyrene spheres. Baking was carried out for 1 hour after 1 day drying. Baking temperatures were 110°C (blue diamond line), 130°C (dotted red line), 150°C (solid green line).
4.6 Porous Oxide Formation

Another anodizing procedure in acid solution was carried out after removing the polystyrene spheres. This step removes controlled amounts of metal from unmasked areas, and forms a porous oxide corrosion product in the reacted metal volume. The current density was recorded versus the time, and a typical result is plotted in Figure 4.23. From the Figure, three general characteristics may be seen. First was the sharp drop of the current density, followed by a current rise to a plateau, and finally another current increase.
Figure 4.23. Current transient during constant potential anodizing of aluminum (solid red line) and aluminum alloy (dashed blue line) at 20V, in 1M sulfuric acid. Deposition of 10 µm carboxylated polystyrene spheres on both samples was from 1.85% (w/v) polystyrene suspension in 30% ethanol; baking was at 130°C for 1 hour; constant current anodizing to 25 V in borate buffer.

The first current rise from the minima and subsequent plateau is typically found during porous anodic oxide formation on Al in acid solutions. The current increase is related to oxide pore formation. On these surfaces without polystyrene spheres, the second current rise
after the plateau is not found. However, as metal removal at unmasked sites resulted in pits with increasing surface area. The increasing surface area on these pits probably accounts for the second current increases in Figure 4.23.

4.7 Pit Arrays Formed by the Polystyrene Template Process

4.7.1 Aluminum Alloy 3003 samples

SEM images of the final pit arrays on aluminum alloy samples are presented in this section. In the optimized process, carboxylated 10 µm polystyrene spheres were used as templates. Deposition was from 1.85% (w/v) suspension in 30% ethanol. Barrier oxide formation was at 1 mA/cm$^2$ to 25 V, and porous anodic oxide formation was at 20 V in 1 M sulfuric acid for 300 s. The oxide was removed by 3 minutes chemical etching with chromic acid stripping solution at 70°C.
Figures 4.24 and 4.25 reveal ordered pit arrays on the alloy surface. The diameter of each pit was close to 8 µm. The center-to-center distance between pits was close to 10 µm within the ordered domains, the same as the diameter of the polystyrene spheres. From Figure 4.24, it can be seen that the circular pits covered most of the area; the arrangement of the cp domains were the same as those of the deposited spheres. The size and spacing of occasional empty areas in the pit arrays qualitatively corresponded to those seen in the polystyrene sphere deposits. Therefore, it is clear that the pit arrays were successfully templated by the polystyrene spheres.
Both figures also indicate that more intermetallic particles are present than after electropolishing. These particles were probably exposed during porous oxide formation or chemical etching. Evidently even though the particles were exposed at the surface by anodizing and etching, they did not interfere with the important steps of porous or barrier oxide formation. High rates of oxygen evolution on intermetallic particles can sometimes prevent anodic film formation. Since this did not occur in the present case, the electrochemistry of the polystyrene templating process was successfully transferred to the 3003 aluminum alloy.
The pit arrays formed on aluminum alloy 3003 surfaces using the caustic etching and polystyrene sphere templating processes can be compared using Figures 4.2-3 and 4.24-25. It is clear that the polystyrene templating method resulted in large improvements of the uniformity of pit structure and spacing.
4.7.2 Aluminum samples

SEM images of pit arrays on Al samples are shown in Figures 4.26 and 4.27, for 3 µm hydroxylated polystyrene and 10 µm carboxylated spheres, respectively.

Figure 4.26. SEM of Al with pit array formed by templating 3 µm hydroxylated polystyrene spheres. Deposition was from 2% (w/v) suspension in 10% ethanol, followed by baking at 115°C for 1 hour. Barrier anodizing at 1 mA/cm² to 25V, and porous oxide formation at 20V were followed by 80 minutes chemical etching in 5 wt% phosphoric acid at 30°C.
Comparison of Figures 4.24-25 with Figures 4.26-27 indicates that the pit arrays formed from 3 and 10 μm spheres were quite different. The arrays formed with 3 μm spheres exhibited ordering only in small domains. Figure 4.26 shows that the diameter of individual pits was close to 2 μm, and the spacing of the pits was 3 μm, which represents the size of the spheres. It can also be seen from Figure 4.26 that the pit depths were larger near their perimeters, suggesting preferential metal removal around the perimeters during porous oxide formation. Figure 4.27 shows that, unlike the samples formed using 3 μm polystyrene spheres, the pit arrays formed using 10 μm polystyrene spheres displayed more ordered arrangements resembling the cp structures of polystyrene deposits. The diameter of individual pits was 6-7 μm, and the spacing between the pits was 9-10 μm, again close to the diameter of the polystyrene spheres.

The pit number density in Figure 4.26 is significantly smaller than that of polystyrene spheres after baking (Figure 4.14). Therefore, the difference of the structures formed using 3 and 10 μm spheres may be partly due to the smaller contact diameter of the small spheres, inferred from the pit diameters (2 μm for 3 μm spheres vs. 6-7 μm for 10 μm spheres). Because of a possibly more secure attachment to the substrate, a smaller fraction of the large spheres may have been detached during growth of the anodic barrier oxide. On the other hand, Asoh et al. reported much larger ordered domains of etched structures formed using 3 μm spheres (54). They did not disclose sufficient details of their fabrication procedures to evaluate the reason for this discrepancy.
Figure 4.27. SEM of Al with pit array formed by templating 10 µm carboxylated polystyrene spheres. Deposition was from 1.85% (w/v) suspension in 30% ethanol, followed by baking at 130°C for 1 hour. Barrier anodizing was at 1 mA/cm² to 25V, and porous oxide formation at 20V were followed by 3 minutes chemical etching in chromic acid at 70°C.
Chapter 5: Conclusion

The formation of ordered microstructure on aluminum alloy 3003, utilizing the colloidal crystal templating method, was studied in this project. Scanning electron microscopy (SEM) and electrochemistry techniques were utilized to study the topography of the formed microstructure and the underlying mechanism of mask formation, which is the basis of the microstructured templating process. The resulting pit arrays for the aluminum alloy 3003 showed typically 6-7 μm in individual pit size, and the spacing between them is 10 μm, the same as the polystyrene sphere diameter. If smaller or larger polystyrene spheres were used, the spacing would be adjusted accordingly.

The flatness of the initial surface of the aluminum alloy 3003 was important for successful template formation. A sufficiently flat surface of aluminum alloy 3003 also could obtained with the same electropolishing method used typically for Al. Longer electropolishing times (7 minutes) are required relative to those used for Al, in order to make the surface of the aluminum alloy suitable for the subsequent anodizing process.

The size of the polystyrene spheres determines the spacing between pits. It also could be noted that the formation or the ordered pits were much easier on the 10 μm polystyrene carboxylate spheres than to the 3 μm polystyrene hydroxylate spheres even with the same treatments and procedures. Ordered pits structures over the entire surface were not produced using the 3 μm spheres, unlike the 10 μm counterparts.
Initial formation of the monolayer close cubic packed (cp) structure of the polystyrene spheres is also essential for the whole process. Several factors were important in determining formation of the cp structure, including the polystyrene spheres solvent, concentration, functionalization, polystyrene sphere size and also the baking temperature.

Polystyrene spheres solvent affect the surface coverage area. Larger droplet coverage containing monolayer spheres could be achieved by reducing surface tension with small additions of ethanol. The concentration of polystyrene in solution also affected the formation of the monolayer cp structures. Suitable concentration of water-ethanol solvent (2% w/v – 30% ethanol) were applied to the 10 µm polystyrene carboxylate spheres in order to avoid the formation of multilayer polystyrene spheres.

In addition to the solvent and concentration of spheres, surface functionalization of the polystyrene spheres also had an effect on the formation of polystyrene particle monolayers. Hydroxyl and carboxyl functionalized spheres were seen to have much higher surface coverage area compared to the unfunctionalized polystyrene spheres. Lastly, baking process was very important in order for successful formation of the ordered pits formation. Baking was carried out to fix the particles in position on the surface of aluminum or 3003 alloy. Without the heating process, detachment of the spheres was observed during anodizing, possibly due to compressive stresses associated with oxide formation. The best temperature was found to be 110°C (1 hour) for the 3 µm polystyrene hydroxylate spheres and 130°C for the 10 µm polystyrene carboxylate spheres. The difference in the optimum baking temperature could be attributed to the differences of particle size, end group, or crosslink density and end group.
Flat substrate surfaces were utilized in this work, however in industrial lithographic process, curved metal surfaces of imaging drums for the substrates in solid-ink technology. The initial deposition of the polystyrene spheres on these surfaces would be critical for successful templating. Possible techniques for the initial stage of the deposition of spheres could include the inkjet printing technique, as explained in Chapter 2. Utilizing this technique, desirable patterns on a substrate could be made in noncontact mode. Thus, with some modifications of the techniques, the transfer of this technique to curved surfaces may be possible.
Chapter 6: References


