MICROSTRUCTURE ALONE INDUCED WETTING TRANSITION FROM HYDROPHILIC TO HYDROPHOBIC ON SILICON AND GRAPHENE

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MICROSTRUCTURE ALONE INDUCED WETTING TRANSITION FROM HYDROPHILIC TO HYDROPHOBIC ON SILICON AND GRAPHENE

By

Henry Louis Ems

A THESIS

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In the present work, transition from hydrophilic to hydrophobic wetting states for an intrinsically hydrophilic surface (contact angle less than 45 degrees) using only surface microstructuring is presented. The surface microstructures are re-entrant microcavities (inverted trapezoidal microstructures) which promote air entrapment below the water droplet causing a Cassie wetting state as opposed to a Wenzel state where the surface is completely wetted. The microstructures were fabricated on a Silicon-On-Insulator (SOI) wafer through steps of deposition, photolithography, etching, and bonding. Contact angle measurements demonstrated the ability of the microfabricated surfaces to sustain large contact angles above 100°, in comparison to a bare Silicon surface which has an intrinsic contact angle around 40°. Energy-dispersive x-ray spectroscopy showed Silicon to be the only chemical element on the surface, meaning free from contaminants that were possible from etching and handling. Optical observations with an inverted microscope hinted to the existence of a Cassie wetting state. In the second part of the thesis, graphene is formed on the inverted trapezoidal microstructures through steps of oxidation, deposition, and thermal evaporation. After fabrication techniques are performed, a thin layer of graphene is left on top of the oxide layer. Using re-entrant microcavities the contact angle transitioned from 77.5 degrees to 91 degrees. Raman Spectra and EDS proved the presence of monolayer graphene and the presence of Nickel, Silicon, and Oxide respectively.
ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

The ability to control the wetting state between a surface and a liquid is very important in many applications, such as heat transfer (e.g., boiling, condensation), microfluidics (e.g., self-propelled droplet), antifouling, and self-cleaning surfaces. The wetting state of a surface is often defined by its equilibrium contact angle with respect to a liquid droplet. In the case of water, a surface is defined as hydrophobic if its contact angle with a water droplet is greater than 90 degrees and is considered hydrophilic if its contact angle is less than 90 degrees. Observations in nature have revealed the extraordinary ability of certain surfaces, such as the lotus leaf, to display a high degree of hydrophobicity though the base material is intrinsically hydrophilic [1, 2]. In an attempt to engineer such surfaces, much research has been carried out to understand the underlying physical mechanisms governing the wetting state of a liquid droplet with respect to a surface. Results have concluded that the wetting state of a surface is dependent on both the chemical composition and the physical topography of the surface [3]. For a smooth and chemically homogeneous surface, the equilibrium contact angle can be computed from the Young’s relation [3] which expresses the contact angle as a function of the relative surface tensions among the solid, liquid and vapor as shown in the equation below:

\[
\cos \theta_E = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}
\]

(1)

where \(\gamma_{SV}\), \(\gamma_{SL}\), and \(\gamma_{LV}\) are the surface tensions of the solid-vapor, solid-liquid, and liquid-vapor interfaces, respectively while \(\theta_E\) is the equilibrium contact angle on a
smooth homogeneous surface [3]. As per Young’s relation, substrates with high surface energy, such as metals, are relatively more hydrophilic than materials with low surface energy, such as many polymers.

In the case of a rough surface, two models have been proposed for the wetting state of a droplet, namely the Wenzel model [4] and the Cassie-Baxter model [5], to describe the macroscopic contact angle of a liquid droplet on a rough surface. A graphical description of these two models is shown in Figure 1-1. As shown on the figure, the Wenzel state assumes that the liquid droplet wets the entire surface. The Cassie-Baxter model, on the other hand, assumes the liquid droplet only partially wets the surface due to air entrapment caused by surface roughness.

The apparent contact angle of a liquid droplet in the Wenzel state can be determined using the Wenzel’s relation:

\[ \cos \theta^* = r \cos \theta_E \]  

(2)

According to the Wenzel’s relation, the surface roughness factor, \( r \), always magnifies the initial wetting properties of a surface. In other words, hydrophobic surfaces will become
more hydrophobic while hydrophilic surfaces become more hydrophilic as surface roughness increases. Therefore, in practical applications, most superhydrophobic surfaces are made from low surface energy materials.

In this study, inverted trapezoidal Silicon microstructures shown in Figure 1-2 have been fabricated using photolithography, etching, and touch bonding to promote a Cassie-Baxter Wetting state by utilizing air entrapment cause by the overhang structures. SEM imaging along wettability testing, and air entrapment investigation were performed.

Figure 1-2: CAD Image of Inverted Trapezoidal Microstructures and Nomenclature Guide

1.1 Related Literature Review

Hydrophobicity from inherently hydrophilic surfaces has been achieved thus far through surface micro-texturing (e.g., micro posts) in addition to being coated with hydrophobic materials [6 - 9]. Surface coatings are, however, unstable at high temperatures and in austere environments, and therefore may not be practical in
applications such as boiling (for enhanced nucleation) and condensation (to promote dropwise condensation).

Recently, it has been discovered and theoretically demonstrated that surface microstructures can lead to hydrophobic surfaces from originally hydrophilic substrates. The observations and results have been explained with the Cassie-Baxter model from which the apparent contact angle can be determined with the following equation:

$$\cos\theta^* = r_f f(\cos\theta_E) + f - 1$$

(3)

Where $r_f$ is the surface roughness factor, and $f$ is the fraction of solid surface area that is in contact with the liquid droplet [8]. The prevalence of the Cassie-Baxter state results from the existence of entrapped air in the microstructures forcing the droplet to sit on a heterogeneous solid-air substrate. Though the Wenzel state is energetically more favorable [10], air entrapment can be promoted by the use of highly engineered microstructures, such as overhang structures, re-entrant textures, or catalyzing etched nanostructures [11 – 17], whereby a Cassie state is achieved through local energy minimums. Though theoretically predicted [18 - 21], the demonstration of hydrophobic surfaces from inherently hydrophilic surfaces, with contact angle less than 45º, using the principle described above, remains to be achieved.

Previously in the literature, wetting transition from hydrophilic to hydrophobic has been achieved on a gold substrate, with an intrinsic contact angle of 70º, using only surface microstructuring [11]. Superoleophobic and oleophobic transitions from inherently oleophilic surfaces have been previously achieved as well [15, 17]. However in the present paper, we demonstrate the transition from hydrophilic to hydrophobic
wetting state of an intrinsically very hydrophilic surface (contact angle less than 45 degrees) using surface microstructuring alone without the use of coating, catalyst, and/or thin film deposition. Both Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) were carried out to characterize the microfabricated surfaces. Contact angle measurements confirmed the hydrophobicity of the fabricated surfaces.
CHAPTER 2
Inverted Trapezoidal Microstructure Fabrication

2.1 Design Parameters and Fabrication

Figure 1-2 shows a schematic illustration of the re-entrant (inverted trapezoidal) microstructures proposed in order to create a hydrophobic surface from an inherently hydrophilic material (Silicon). Various dimensions (Table 0-1) of the cavity base and array pitch were considered to investigate the impacts of design parameters on the surfaces’ wettability. The sidewall angle of the inverted trapezoids is set by a potassium hydroxide (KOH) anisotropic wet etch used to produce the microstructures. The height of the microstructures is kept the same at 10 microns. By setting the width at the beginning of the etch along with the height of the microstructures the smaller width of the trapezoid is set.

Table 0-1: Microstructure Design Parameters

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Width - W (µm)</th>
<th>Height - H (µm)</th>
<th>Pitch - P (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>20</td>
<td>10</td>
<td>35</td>
</tr>
<tr>
<td>S2</td>
<td>25</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>S3</td>
<td>30</td>
<td>10</td>
<td>65</td>
</tr>
<tr>
<td>S4</td>
<td>20</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>S5</td>
<td>25</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>S6</td>
<td>30</td>
<td>10</td>
<td>55</td>
</tr>
</tbody>
</table>

Based on the proposed design, the microstructured surfaces were then fabricated using MEMS and microelectronics fabrication techniques. The microelectronic fabrication techniques involved can be summarized in a series of processes which consists of thin film deposition, photolithography, etching, and boxing. Figure 0-1 shows
a flow diagram of the microfabrication process used to fabricated the inverted trapezoidal microstructures on a Silicon substrate. Included with the figure is a detailed explanation into the various steps performed. Fabrication of the microstructures was carried out at the Cornell NanoScale Facility.

Surfaces were fabricated from a 100 mm diameter Silicon-on-Insulator (SOI) wafer (Ultrasil, double-side-polished, orientation <1-0-0>, device layer = 10 µm, Buried Oxide (BOX) = 1 µm and handle wafer = 525 µm). All surface variances were fabricated on the same wafer, hence they all had the same microstructure height, namely the thickness of the SOI wafer device layer ~ 10 µm Error! Reference source not found.a. Before the KOH etch, a low stress 100 nm LPCVD Silicon nitride film was deposited (800 ºC, 200 mT, 40 minutes, flow rate of 126 sccms DCS and 22 sccms NH3) on both sides of the SOI wafer to serve as KOH etch mask, Figure 0-1b.

Patterning of the NH3 layer was done using a S1813 Shipley resist (1.5 µm thickness). Exposure for the resist was at ~10 mW/cm² for 4.5 seconds. Reactive Ion Etching (RIE) using CF₄ completed the patterning process detailed in Error! Reference source not found.c. Angled sidewalls of the microstructures were achieved through a Potassium Hydroxide etch (50 % KOH, 18 min, 70 ºC), etching through the device layer up to the buried oxide which is shown in Figure 0-1d. Figure 0-2 shows the catwalk structures formed after the KOH anisotropic etch. The KOH etch creates a trapezoid with an angle of 54.7º at the base as measured using an SEM (Figure 0-3c).
Figure 0-1: Fabrication Steps

(a) 
(b) 
(c) 
(d) 
(e) 
(f) 
(g)

Silicon Nitride
Silicon Dioxide
Silicon

Figure 0-2: "Catwalk Structures" After KOH Etching
Following KOH etching, Nitride striping, Error! Reference source not found.e, and cleaning, the wafer was cut into individual chips, and each manually “touch” or fusion bonded with a separate Silicon chip. The chips were then placed in an oven and annealed overnight, Figure 0-1f, after bonding and annealing, Deep Reactive Ion Etching (DRIE) and Hydrofluoric Acid (HF) etching were used to etch the handle wafer and the buried oxide, respectively. Figure 0-3 shows SEM images of the re-entrant microcavities microstructures. As can be seen on Figure 0-3, the surface consists of an array of square re-entrant microcavities with the small opening at the top and the larger opening at the base. The cross section view of the Silicon re-entrant microcavities was obtained by scoring one of the samples with a diamond point and then breaking the chip at the scored area. Actual dimension of the re-entrant microcavities can be seen on Figure 0-3c.
2.2 Surface Characterization

As stated in the introduction, the wetting state of a surface is a function of both its chemical and physical properties. Therefore, it is very important to understand the chemical composition of the microfabricated surfaces to have a full understanding of its wetting properties. Through the microfabrication processes, the surfaces were exposed to many chemicals, leaving the samples at risk for possible contamination. To demonstrate that Silicon is the only element still present on the microfabricated structures, surface
characterizations were carried out on the samples using Energy-dispersive X-ray spectroscopy (EDX). Figure 0-4 presents the results of the EDX measurements, confirming that the only element present on the samples after fabrication was Silicon (Si), though there may be small traces of native oxide (also present on the bare Silicon surface). The inset images in Error! Reference source not found. indicate the location where the EDX measurements were taken, namely inside and outside of the re-entrant microcavities.

Contact angle measurements using DI water (72 mN m⁻¹) were carried out to characterize the wettability of the microfabricated surfaces; results of the measurements are tabulated in Table 0-2. As can be seen from the data, dimensional variations (pitch, width) on the microstructured surfaces (i.e. S1 - S6) have little to no effects on the macroscopic contact angle. However, the most important observation is the increase in contact angle from the bare Silicon surface to the microfabricated Silicon surfaces. The bare Silicon surface is intrinsically very hydrophilic with a contact angle of around 40° while all the microfabricated Silicon surfaces become hydrophobic with contact angles ranging from 93° to 101°. This experiment demonstrates microstructure-alone induced transition from hydrophilic to hydrophobic wetting state on Silicon. Measured contact angle hysteresis felt between 30° and 40°, this is however relatively consistent with previously published literature [22].

Figure 0-5 shows visible difference in contact angle between the bare Silicon and one of the microfabricated surfaces. Liquid droplets on the microstructured surfaces are believed to be sitting in the Cassie state, which has possibility for contact angle shifts above 90° from hydrophilic. The observed wetting transition from hydrophilic to
hydrophobic is attributed to entrapped air within the re-entrant microcavities, which causes an upward force (energy barrier) on the droplet, leading to an increased contact angle and a transition to a Cassie-Baxter wetting state. This phenomenon has been previously predicted through modeling [1] and demonstrated for relatively large intrinsic contact angles (~ 74 degrees) with a hydrogen terminated Silicon surface. Cassie wetting state of overhang structures has been also attributed to capillary forces which prevent total wetting of the surface [13, 14].
Figure 0-4: EDX Results
To study the stability of the microstructures in sustaining a Cassie state, we carried out contact angle measurements on the S3 surface with increasing droplet size, 5 μL to 50 μL and images up till 125 μL. Values for the contact angles with increasing droplet size are included in Table 0-3. Over this range of droplet sizes, no apparent change in wetting state was observed. At a certain droplet size the gravity will take effect however that limit was not reached at the maximum of 50 μL.
Table 0-3: Contact Angle Measurements With Increasing Droplet Size on Sample S3

<table>
<thead>
<tr>
<th>Droplet Size (μL)</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>96</td>
</tr>
<tr>
<td>10</td>
<td>98</td>
</tr>
<tr>
<td>20</td>
<td>97</td>
</tr>
<tr>
<td>30</td>
<td>98</td>
</tr>
<tr>
<td>40</td>
<td>95</td>
</tr>
<tr>
<td>50</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 0-4: Sample Solid Fractions

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.38</td>
</tr>
<tr>
<td>S2</td>
<td>0.43</td>
</tr>
<tr>
<td>S3</td>
<td>0.47</td>
</tr>
<tr>
<td>S4</td>
<td>0.34</td>
</tr>
<tr>
<td>S5</td>
<td>0.40</td>
</tr>
<tr>
<td>S6</td>
<td>0.41</td>
</tr>
</tbody>
</table>
Table 0-4 shows the solid fractions for the various samples investigated. A plot of the measured contact angle as a function of solid fraction is shown in Figure 0-6. As shown in the Cassie-Baxter equation previously discussed as the solid fraction decreases and more water is exposed to air the contact angle will continue to increase.
As shown on the Figure 0-7, the Cassie-Baxter model predicts relatively well the experimental data for high solid fractions. For lower solid fractions (e.g., samples S4 and S1), the Cassie-Baxter model significantly under predicts the experimental data. One explanation for the error is the possibility of sagging, which would increase the radius of curvature of the droplet increasing the solid fraction and decreasing the contact angle.

The increasing droplet size data for Sample S3, Table 0-3, is plotted in Figure 8 and displays similar trends in being slightly under the predicted contact angle. Due to the small variation in measured contact angles for Table 0-3 the values line up almost on top of one another at the $f=0.47$ position. The inset image shows the variation between the S3 sample measurements over various droplet sizes.
In order to get more insight into the wetting state of a droplet on the microstructures and the existence of air entrapment, optical microscopy was utilized to visualize the nature of a liquid droplet on the re-entrant microcavities’ surfaces. Figure 9 shows a schematic drawing of the experimental setup used to carry out the above-mentioned qualitative investigation. Figure 0-8 (left) shows a cartoonish cross-sectional view of a liquid the droplet being forced to sit in a Wenzel state using a glass slide (i.e. the applied force). In this experiment, we are interested in visualizing the droplet state before, during, and after the application of the glass slide. In order to visualize wetting state under a droplet, the re-entrant microcavities were bonded to a transparent Pyrex wafer instead of a Silicon wafer in the step shown in Figure 0-1f. With a Nikon Eclipse Ti inverted microscope (Figure 0-8 (right)), the liquid droplet wetting state was visualized from the bottom of the surface through the Pyrex. Using a hydrophobic coated microscope slide, pressure was applied onto a liquid droplet sitting on the re-entrant
microcavities, and optical images were taken before, during, and after the application of pressure. Figure 0-9 shows results from the visualization experiments.

![Figure 0-9: Wetting Visualization Results](image)

Without any applied pressure, the liquid droplet sits on the re-entrant microcavities in a Cassie Baxter state. Because of the existence of a liquid/air interface and the relatively thick layer of air underneath the droplet, light transmittance across the sample in the Cassie Baxter state is expected to be different from when the droplet is in the Wenzel state due to light diffraction and scattering. This is exactly what we observed when we compared the microscope images before and during pressure application on the droplet. With the droplet in the Wenzel state (Error! Reference source not found., middle column), the images showed darker and star-like diffraction patterns, perhaps owing to the diffuse nature of the light across the liquid droplet. This is in contrast to images when the droplet was in the Cassie-Baxter state where the liquid/air interface could possibly act as a lens, concentrating light into brighter spots. The reduction in air area is attributed to the compression of the air caused by the force applied above. Some air may also dissolve
into the water droplet or/and escape from the top as well as the bottom from small cracks in the substrate. With the applied pressure removed, the droplet partially returns to its Cassie-Baxter state, resulting in diffraction patterns somewhere between a full Cassie-Baxter state and a Wenzel state. The partial return of the droplet back to the Cassie-Baxter state is hypothesized to be caused by the force of the compressed air acting against the droplet after the force on the glass is removed as also previously hypothesized by other researchers [20]. During the experiments, care was taken to account for the effects of the microscope slide used to apply pressure on the droplet. The proposed mechanism shown in Error! Reference source not found. is at this stage a simple stipulation/theory; however further work is needed to validate it.

2.3 Surface Condensation

After verification of the hydrophobicity of the surface, condensation experiments were carried out on the fabricated surfaces. Previous literature has examined the use of hydrophobic surfaces, which have been proven to lower the freezing point of water as well as decrease ice adherence to the microstructured surface [23, 24]. Condensation can appear in two forms: film condensation, which is shown in Figure 0-10 (Left) on an oxidized surface, and dropwise condensation, which is shown in Figure 0-10 (Right) on an inverted trapezoidal microstructured surface. Industrial applications, such as heat exchangers, benefit from dropwise condensation because of the higher transfer coefficients when compared to filmwise condensation.
Condensation on the inverted trapezoidal Silicon structures was observed with an optical microscope. The sample was cooled below 0° C via chilled anti-freeze fluid flowing through the metal stage upon which the sample was sitting. Images were taken as droplets began to nucleate on the sample. It was observed that the droplets would coalesce around the cavities, as opposed to over the cavities, as long as the droplets were still smaller than the size of the cavities. Figure 0-11 shows the coalescence of droplets that formed around the cavities. The cavities appear to cause an upward force which will alter the radius of the droplets on the surface, causing a bend around the cavity; this is most evident in the red circular region of the optical image. In Figure 0-12, a more detailed analysis of the dropwise formation of condensation on the surface is displayed. Again, the drops continued to form around the cavities, bending to cover the top surface, as opposed to forming over the cavities.
Figure 0-11: Coalescence of Droplet around the Cavity

Figure 0-12: Droplet Formation
CHAPTER 3

Graphene Introduction

Recently, graphene has become a topic of interest because of its electrical [25-30], mechanical [31, 32], thermal [33], and optical [28, 34] properties, and is becoming a viable option for addressing size and temperature concerns for future electronics. Graphene is classified as an atomic layer of sp², covalently bonded, carbon atoms in a 2-dimensional honeycomb lattice structure [27, 31]. Because of the reduced thickness compared to other material layers, graphene presents an ideal substitute in small scale applications, namely MEMS devices. Such MEMS devices include gas sensors which, when using graphene, have proven to be sufficiently sensitive and have increased potential for mass production [29].

Graphene has also been proven as a viable alternative in terms of heat diffusion. While copper remains a popular heat sink in electronics with a thermal conductivity ranging in the order of ~400 W/m*K, graphene can be a viable option because of a larger thermal conductivity of ~600 W/m*K [33]. Monolayer graphene is particularly desirable because of the high carrier mobility of around 15000 cm²/V*S. One typical method of graphene fabrication calls for chemical vapor deposition (CVD) and etching before being moved to a dielectric substrate [35, 36]. Another method proposed is the direct spray coating of 3D microstructures and micromechanical cleavage [37-39]. Spray coating has been proven to cover the entire surface of SU-8 micropillars; while the coating was not uniform in thickness, the graphene was still proven to increase electrochemical sensing
Etching can leave the graphene cracked, degraded, or contaminated. Typical etched graphene can also display high sheet resistance in the order of 2000 to 5000 Ω/sq [25].

### 3.1 Graphene Related Literature Review

Hydrophobic graphene has thus far been achieved by varying the substrate beneath the graphene most notably SiC which has led to a measured contact angle between 90-95° [40-42]. Previous research has relied on chemical solutions along with graphene to coat superhydrophobic surfaces with contact angle around 162° when using ethanol. These dip coating processes have proven time intensive, with multiple coatings and drying cycles needed to fabricate the surface [41]. One popular mode of graphene fabrication is chemical vapor deposition of graphene along with enhancement onto a surface/substrate [43-45]. Copper surfaces have previously proven to increase the heat transfer properties as well as promote dropwise condensation; however, copper grains were still visible below the graphene surface and did not exhibit an evenly dispersed graphene coating, though the graphene coating covered a majority of the surface [43]. Plasma enhanced chemical vapor deposition along with M. Alternifolia precursor led to a contact angle around 135°. Though the contact angle with graphene was large, increased surface roughness was caused from the strain induced during growth, leading to a lower transmittance in the 85% level [44]. Chemical enhancement after the initial growth of graphene has proven effective in obtaining superhydrophobic surfaces [41, 45, 46, 47].
CHAPTER 4
Graphene Fabrication and Characterization

4.1 Graphene Fabrication

Under the assistance of the Laser Assisted Nano Engineering Lab at the University of Nebraska-Lincoln, graphene was fabricated on the inverted trapezoidal microstructures. Thermal oxidation was performed on the inverted trapezoidal Silicon microstructures for 40 hours at 1000 °C. After thermal oxidation, the thickness was measured using a reflective film thickness measurement system (Filmetrics F40) in the Nebraska Center for Materials and Nanoscience (NCMN) facility at the University of Nebraska-Lincoln, as shown in Figure 4-1. The oxide thickness was determined to be 580 nm, which was thick enough to prevent the nickel that would later be deposited from reacting with the pure Silicon below.
Using sputtering deposition, layers of carbon and nickel were deposited onto the microstructures. The thickness of the carbon layer was 5 nm and the nickel film was fixed at 65 nm shown in Figure 4-2B. The thicknesses of the films were investigated by Wei Xiong et al. in “Single-Step Formation of Graphene on Dielectric Surfaces” with the fabrication techniques being highlighted in Figure 4-3 [25]. After deposition of the
carbon and nickel, thermal evaporation was performed on the surface to evaporate the nickel layer. The evaporation was performed at 1100 °C for 2 minutes, leaving graphene on the SiO2 surface. The fabrication of the graphene is displayed in Figure 4-2C.

![Figure 4-2: Graphene Fabrication Diagram](image)

![Figure 4-3: 3-D Graphene Fabrication Diagram [25]](image)
4.2 Graphene Characterization

Following the fabrication of the film, Raman spectroscopy was used to investigate the type of graphene formed on the surface. The Raman spectrum exhibited peaks at the 2D, G, and D band around 2700, 1582, and 1357 cm\(^{-1}\) positions, respectively. Monolayer graphene is typically classified by having a I\(_{2D}/I_G\) ratio that is >1.4, while bilayer graphene is classified between 0.8 and 1.4, and finally three graphene layers classified for a ratio below 0.8. A flat SiO\(_2\) sample was coated using the exact same fabrication methods in order to compare it with the coated inverted trapezoidal structure. Figure 4-4 shows the Raman spectrum for the microstructured sample that was fabricated with graphene. By taking the area under the curve for the I\(_{2D}\) and I\(_G\) bands for the microstructured sample the sample had an I\(_{2D}/I_G\) ratio of \(\sim 2.7\), well above the limit for the consideration of monolayer graphene.

![Figure 4-4: Raman Spectrum for Microstructured Sample](image-url)
SEM images were taken to visually inspect the graphene grown on the surface. Images from the pure Silicon microstructured sample were compared to the microstructured sample with the graphene present after fabrication. Figure 4-5 shows Sample 1 before any oxidation or graphene fabrication in the top left portion, while the top right and bottom images in Figure 4-5 are SEM images after the fabrication of graphene on the surface. The tilted image in the bottom right shows increased height in the Z-direction of the graphene as opposed to initial hypothesis of a honeycomb 2-D structure forming. The non-tilted images of the graphene microstructured sample show the variation in the graphene formation at the edge of the cavity in comparison to the areas between cavities. At smaller magnifications the graphene seems to form uniformly, not varying in either the X or Y direction.
Energy-dispersive X-ray spectroscopy (EDX) was performed using the Helios electron microscope at the University of Nebraska-Lincoln. Measurements were performed at multiple spots around the microstructured surface, as shown in Figure 4-6. The spots were chosen due to the visible differences between the surrounding area (Selected Area 1) and the area immediately next to the cavity (Selected Area 2). After graphene fabrication, it was assumed that the only elements present on the surface were carbon, nickel, SiO₂, and Silicon. EDX was used to investigate the amount of carbon and nickel present in weight and atomic percentages, but also to confirm that contaminants from handling and deposition were not present.
EDX results for Area One are given in Figure 4-7 and Table 4-1. Due to the depth of the scan, considerable amounts of Silicon were found as film layers are less than 1 micron total. The scan revealed carbon element on the surface of the sample along with residual nickel. The presence of residual nickel could be from variability in sputtering as well as thermal evaporation inconsistencies. The error percentages listed are based on the percent of the weight percentage and not an overall numerical value. Based on the atomic percentage, there was over five times as much carbon as nickel.
EDX results, shown below in Figure 4-8 and Table 4-2, Area Two show increased amounts of nickel present along to the edge of the cavity for the microstructures. This can account for the visible increase in height of the overall surface microstructures for the graphene. Spacing and disconnections of the graphene can be caused by the increase in the height of the structures due to the excess Nickel present. As with Area One, large amounts of oxide and Silicon were present from the depth of the
scan and considerable larger size of the oxide film compared to nickel and carbon films that were sputtered.

![Figure 4-8: EDX Count Results for Area Two](image)

**Table 4-2: EDX Percentage Results Area Two**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>2.19</td>
<td>4.06</td>
<td>27.44</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>33.06</td>
<td>46.06</td>
<td>9.03</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>61.12</td>
<td>48.50</td>
<td>2.73</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>3.62</td>
<td>1.38</td>
<td>12.07</td>
</tr>
</tbody>
</table>

Being able to change the wettability of monolayer graphene on Silicon using microstructures would prolong the lifetime of the surface. Thermal evaporation of the graphene can also serve as a long term solution as opposed to chemical etching which can lead to degraded graphene and contamination possibilities. Contact angle measurements, shown in Table 4-1, of the graphene on the inverted trapezoidal Silicon microstructures
as well as on a flat Silicon chip were compared to view the change wettability caused by the structures. The flat graphene sample averaged a contact angle around 77.5°. The microstructured sample had a contact angle average of 91°, which is just above the 90° threshold to be considered hydrophobic. Previous Silicon microstructures had a contact angle around 100° before graphene fabrication. One possible explanation for the decrease in the contact angle between microstructures samples is the presence of the oxide in the graphene sample. The oxide with its typical hydrophilic behavior can cause a hydrophilic influence to the surface negating some of the decreasing wettability influence that is caused by the graphene and nickel present along with the microstructures.

Table 4-3: Contact Angle Measurements

<table>
<thead>
<tr>
<th>Measurement Number</th>
<th>Graphene + Microstructures [Degrees]</th>
<th>Graphene [Degrees]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90.92</td>
<td>78.16</td>
</tr>
<tr>
<td>2</td>
<td>91.89</td>
<td>76.24</td>
</tr>
<tr>
<td>3</td>
<td>88.99</td>
<td>76.64</td>
</tr>
<tr>
<td>4</td>
<td>92.09</td>
<td>79.2</td>
</tr>
</tbody>
</table>

The presence of Silicon is because of the depth of the scan being performed. While levels can be varied to not measure as deep it was determined that the accuracy and overall better scans was desired. The flat Silicon sample proved to contain similar results, with carbon around an atomic percentage of 9.87% and nickel around 1.69%. 
4.3 Nickel Etching

As previously stated, there was a considerable amount of residual nickel that was left after initial fabrication took place. After fabrication, a Nickel Etchant Type I, Transene Company Inc. was used to remove the excess nickel. After nickel etching the roughness of the sample decreased significantly, as shown in the transition from the graphene and nickel SEM in Figure 4-9 to the bottom right image in Figure 4-9. There was a small decrease in graphene content, though a majority of the material etched is nickel.
Figure 4-10 shows the investigated areas for the EDX measurements. Similar to previous EDX measurements the spots of interest were chosen because of the visible difference near the edge of the cavity. The two areas showed very small differences in element composition. The biggest difference was the dramatic decrease in nickel present, <0.5% in atomic percent in both cases. There was a small change in atomic percentage for the
carbon. It is highly likely that some of the carbon was etched away during the nickel etching process. No other elements were detected from the etching and handling processes.

Figure 4-10: EDX of Nickel Etched Graphene
Table 4-4: EDX Results Middle Section

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>2.09</td>
<td>3.92</td>
<td>35.73</td>
</tr>
<tr>
<td>O K</td>
<td>29.41</td>
<td>41.37</td>
<td>9.65</td>
</tr>
<tr>
<td>SiK</td>
<td>68.05</td>
<td>54.54</td>
<td>2.33</td>
</tr>
<tr>
<td>NiK</td>
<td>0.45</td>
<td>0.17</td>
<td>58.19</td>
</tr>
</tbody>
</table>

Table 4-5: EDX Cavity Edge

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>2.05</td>
<td>3.71</td>
<td>39.56</td>
</tr>
<tr>
<td>O K</td>
<td>35.8</td>
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<tr>
<td>SiK</td>
<td>60.87</td>
<td>47.14</td>
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<tr>
<td>NiK</td>
<td>1.28</td>
<td>0.48</td>
<td>31.65</td>
</tr>
</tbody>
</table>

Contact angle measurements after the Nickel etching ranged between 70° and 100°. Positions for the measurements were distributed uniformly over the microstructure sample. The variable wetting was attributed to more random distributions of carbon on the surface with some influence still from the oxide layer below.
CHAPTER 5

Conclusion

In the work presented a novel technique for microstructure-alone induced transition from hydrophilic to hydrophobic wetting state of an inherently hydrophilic surface is presented with Silicon. Using microfabrication techniques including thin film deposition, photolithography, etching, and bonding inverted trapezoidal microstructures on Silicon are fabricated.

Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) were carried out to characterize the microstructured surfaces. SEM images confirmed that the design parameters of height, width, and pitch were met. EDX results confirmed that Silicon was the only element present on the surface, making it free from contamination that was possible during fabrication and handling.

Contact angle measurements showed the ability of the surface to induce a Cassie-Baxter wetting states with a liquid droplet on the surface, with contact angles over 90° whereas bare Silicon was measured to have a contact angle of 40°. Therefor it is experimentally shown the ability to fabricate a hydrophobic surface from a substrate with a low intrinsic contact angle (~40°). It was found that there was no significant difference between contact angles for droplet volumes between 5 to 50 μL. Contact angle modeling using the Cassie-Baxter wetting equation showed relative agreement between model contact angles and the measured experimental values. Images obtained using an inverted microscope indicated that droplets sitting on the microcavities are in the Cassie-Baxter wetting state. Condensation experiments showed the microfabricated surfaces ability to promote dropwise condensation as opposed to filmwise condensation. During the
condensation experiment droplets formed from the decrease in temperature and tended to form around the cavities during coalescence until they are able to move completely over the cavity.

Next monolayer graphene was fabricated on the surface of the inverted trapezoidal Silicon microstructures. The graphene was fabricated using oxidation, film deposition of Carbon and Nickel, and finally thermal evaporation. The fabrication technique allows for a uniform coating without the use of chemical etching to transfer the graphene. Raman Spectrum, SEM, and EDX testing were used to characterize the surface. Raman Spectrum confirmed the presence of monolayer graphene with an $I_{2D}/I_G$ ratio of roughly 2.7. SEM imaging and EDX confirmed the graphene coated the entire structure with no other contaminants on the surface. SEM and EDX results also showed the presence of excess Nickel that was not thermally evaporated during fabrication. Contact angle measurements confirmed a shift from an equilibrium contact angle of around 77.5° to a microstructured graphene contact angle of around 91°. The smaller shift was attributed to the presence of Oxide and residual Nickel on the surface. After etching the residual Nickel away, SEM imaging confirmed a more 2D layer of graphene on the surface along with a decrease in Nickel percentages confirmed by the EDX testing. Contact angle measurements ranged between 70° to 100°, showing more wetting variability after Nickel etching.
REFERENCES

A

APPENDIX

A.1 Inverted Trapezoidal Microstructure Information

Full design parameters are given below in Table A-1. As shown before the height was kept the same however the width and center to center distance was varied. Some samples had been damaged during transfer from Cornell to Nebraska and were not included in testing.

Table A-1: Design Parameters

<table>
<thead>
<tr>
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<td>5.839</td>
<td>19.6</td>
<td>3.761</td>
<td>54.7</td>
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</table>

Figure A-1 shows a comparison between a droplet on a Silicon wafer and a droplet on a microstructured sample. As discussed previously the droplet on the Silicon wafer will spread out wetting in the Wenzel state while the microstructured sample is in the Cassie-Baxter state leading to an increased contact angle.
Figure A-1: Droplet Comparison on Flat Silicon and Microstructured Silicon

Figure A-2 shows dimensioned images of the microstructured sample. The dimensions via the SEM are helpful in insuring that the design parameters were matched during fabrication.

Figure A-2: Top View SEMs of Inverted Trapezoidal Microstructures on Silicon
Table A-2: 1μL Contact Angle Results

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<th>SAMPLE</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
<th>Trial 5</th>
<th>Trial 6</th>
<th>Trial 7</th>
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<th>Std Dev</th>
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<td>99.13</td>
<td>98.58</td>
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<td>98.17</td>
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<td>93.66</td>
<td>94.98</td>
<td>94.15</td>
<td>95.92</td>
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<td>3.07</td>
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<td>100.64</td>
<td>99.69</td>
<td>100.31</td>
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<td>107.41</td>
<td>112.99</td>
<td>107.91</td>
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<td>5.23</td>
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<td>39.38</td>
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Table A-2 gives the complete contact angle measurements for 1 μL droplets while Table A-3 for 2 μL measurements, all performed during the wetting characterization. Tables A-2 and A-3 shows the contact angle varying between 90°-112°, showing the shift to the hydrophobic wetting state.

Table A-3: 2μL Contact Angle Results

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
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<th>Trial 7</th>
<th>AVERAGE</th>
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<td>38.57</td>
<td>39.38</td>
<td>39.38</td>
<td>1.07</td>
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</table>
Figure A-3 shows the measurement of contact angle over varying droplet sizes. As the droplets increased beyond 60 μL the droplets were no longer visible using the camera for contact angle measurements so outside images had to be taken.

![Contact Angle Progression on Microstructured Silicon](image)

A.2 EDX Results on Flat Graphene Silicon Sample

Figure A-4 gives the area for investigation for the flat graphene sample on silicon. Figure A-5 shows the EDX results for the flat graphene sample along with the numerical results in Table A-4. Similar to before there was a substantial amount of Nickel residue.
however there was a larger atomic percentage of graphene as compared to the microstructured sample. Raman Spectrum in Figure A-6 shows the expected peaks at the various 2D, G, and D bands as expected. The peak for the 2D band was not as high as what would be expected.

Figure A-5: EDX Flat Silicon Results

Table A-4: EDX Flat Silicon

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>5.23</td>
<td>9.87</td>
<td>14.93</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>25.32</td>
<td>35.89</td>
<td>9.08</td>
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<tr>
<td>Silicon (Si)</td>
<td>65.08</td>
<td>52.55</td>
<td>2.48</td>
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<tr>
<td>Nickel (Ni)</td>
<td>4.38</td>
<td>1.69</td>
<td>5.36</td>
</tr>
</tbody>
</table>
Figure A-6: Raman Spectrum for Flat Silicon
A.3 Contact Angle Modeling Program

%%% Contact angle modeling of inverted trapezoidal silicon microstructures

%%% Original Contact Angle
Contact_Angle_Original=40*((2*pi())/360);

%%% Dimensions
center=65;
height=10;

%%% Etching Angle Via SEM Dimensions
theta=atan(height/((17.48-5.42)/2));
theta_deg=theta*(360/(2*pi()));

%%% Designed width dimension
width=30;
a=10/(tan(theta));
b=(width/2)-a;
R=1.0*(b*cos(theta));
R=R+((center/100)*(20));
top=center-(2*b);
deg=theta*(360/(2*pi()));
f_first_top=top+(0.0*R);
f_first_bottom=(top+(0.0*R)+((pi()/180)*(180-(2*deg))*1.0*R));
%f_first=f_first_top/(f_first_bottom)
f_first=(f_first_top)/(f_first_bottom)
f_second=((pi()/180)*(180-(2*deg))*1.0*R)/((center-(2*b))+(2*(10/sin(theta)))+width);
%f_second=1-f_first
Contact_Angle_New_Radians=acos((f_first*cos(Contact_Angle_Original))-f_second);
Contact_Angle_New=Contact_Angle_New_Radians*(360/(2*pi()));
Contact_angleCassie=(f_first*cos(Contact_Angle_Original))-(1-f_first);
ContactAngleDegreesCassie=acos(Contact_angleCassie)*(360/(2*pi()));
ContactAngle=(ContactAngleDegreesCassie+Contact_Angle_New)/2