1. Introduction
Textured superhydrophobic surfaces have, over the past few years, been heavily scrutinized for applications involving the improvement of efficiency – namely enhancement of heat transfer in boiling processes, reduction of drag associated with liquid flows near boundaries due to no-slip conditions and dropwise condensation processes. Extensive study of these surfaces has however revealed a lack of robustness in terms of performance. One key example is the increase of superheat required for boiling once trapped air or gas diffuses out of the cavities of textures surfaces. A potential solution lies in predicting parameters for vapor stabilizing surfaces – textured substrates with theoretically driven feature design, such that it is thermodynamically favorable for a liquid to spontaneously produce vapor to fill roughness grooves on the substrate [1], in the absence of or preferential diffusion away of an environmental gas [2]. By designing specific surface geometries, such surfaces have been theoretically shown to exist and it is our goal to experimentally verify their existence.

2. Samples
Samples for performing experiments were obtained from several sources. The group of Professor Constantine Megaridis at the University of Illinois, Chicago provided one set of samples used for several experiments. Their method of fabrication of these surfaces involved spray coating of a combination of fluoropolymer blend dispersions and filler particles that provided surface texture [3]. By using a novel combination of several fluoropolymers such as poly(vinylidene fluoride) (PVDF), perfluoroalkyl methacrylate copolymers (PMCs) etc. surfaces were obtained that are environmentally friendly, water dispersed agents and are approved for industrial use, while still providing a high contact angle of 110° when coated on an untextured surface. The filler particles consisting of organic nanoclay, provided the coating nanostructured surface with a high aspect ratio that can be controlled depending on the particle size distribution. The advantages of this technique include the ability to produce superhydrophobic surfaces of varying critical dimensions over large surface areas and varying substrates.

While the aforementioned samples had large surface areas on a variety of substrates, the surfaces essentially consisted of a randomly distributed aggregation of nanoparticles. Since the theory is based on the analysis of a single cavity, the ability to fabricate samples consisting of a surface with highly defined nanostructured features was essential. Structures sizes were required to be on the order of hundreds of nanometers, which precluded the use of conventional optical lithography where feature sizes are limited to approximately 1 μm. Using the SANE method, the lab of Professor Teri Odom at Northwestern University was able to produce highly ordered nanostructures in silicon of varying dimensions [4] (Figure 1). Several methods were investigated to impart the silicon surface with a high contact angle. A deposition of a final layer of octofluorocyclobutane (C₈F₈) during a Deep Reactive Ion Etching (DRIE) Bosch Process step was employed for this purpose to obtain flat surfaces with contact angles of 111.2°. The theory was then modified for surfaces matching those in the experiments and a variety of samples of varying feature sizes were obtained.

3. Experimental Methods and Results

3.1. Roll-Off Angle Experiments
To verify the dependence of surfaces with above critical feature size we performed a modified version of a common test used to test the dynamic hydrophobicity of a sample – the roll-off angle test [5, 6]. In this test a liquid
A droplet of a fixed volume is gently placed on the surface which is initially parallel to the ground. The surface is subsequently tilted to the point at which the component of the weight of the droplet parallel to the surface overcomes the forces of adhesion at the surface. In each case it is ensured that the test is started at a fixed period of time after the droplet is placed on the surface. Advanced systems use high speed cameras to measure the advancing and receding contact angles at the point of roll-off [7].

With an aim to analyze the dependence of the hydrophobicity of a particular surface on ambient air, roll-off angle experiments as described above were performed at ambient pressure and at vacuum. It was hypothesized that a surface with features small enough to be vapor stabilizing would show little to no change in roll-off angle when the droplet was subjected to a vacuum, whereas a non-vapor stabilizing surface would show a significant increase in roll-off angle when exposed to an environment devoid of air.

To perform this experiment the samples were placed in a bell jar attached to a vacuum pump. At vacuum condition the pressure was 610 mm Hg vacuum. The substrates used for these experiments were provided by the Megaridis group and had feature sizes of 10 nm and 250 nm on an aluminum substrate. Even in the case of experiments performed at ambient pressure the droplet was placed on the surface and an interval of 2.5 minutes (corresponding to the period required for the vacuum pump to reach pressure) was allowed before the experiment was started. A micropipette was used to obtain a droplet of 10 μl for each experiment. An optical analysis of the droplets exposed to vacuum for the duration of the experiment showed no noticeable reduction in volume (measured using diameter of the beaded droplet on the superhydrophobic surface) due to evaporation.

The results obtained for the conditions and samples are summarized in Table 1. For each condition at least 25 data points were recorded to obtain the results. As expected the surface with the 10 nm feature size had almost no change in the roll-off angle while the surface with the 250 nm feature size showed a greater than two-fold increase in contact angle under vacuum. This is a clear indication of the dependence of a surface with a larger feature size on the presence of air or an external gas in order to maintain its self-cleaning property. This conclusion was supported by further experiments described in section 3.2.

<table>
<thead>
<tr>
<th>Feature Size</th>
<th>Ambient Pressure</th>
<th>Vacuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 nm</td>
<td>3.70° (σ = 1.51°)</td>
<td>3.61° (σ = 1.66°)</td>
</tr>
<tr>
<td>250 nm</td>
<td>10.94° (σ = 3.85°)</td>
<td>22.04° (σ = 7.98°)</td>
</tr>
</tbody>
</table>

Table 1: Average roll-off angle with standard deviation for 10 nm and 250 nm surfaces at ambient pressure and vacuum conditions.

### 3.2. Aging Experiments

A factor for superhydrophobic surfaces that is particularly important for phenomena such as boiling and liquid drag is the performance of the surface when wholly submerged underwater [8, 9]. The sustainability of a gaseous layer or gas pockets over a long period of time is essential to the preservation of the drag reducing nature of these surfaces. For example, the reduction in drag is due to the presence of low viscosity gas between the liquid and the solid substrate. Superhydrophobic surfaces that have been studied to date have shown a tendency to lose this property over time [10] and transition from a favorable “Cassie” state to the less favorable “Wenzel” state, in which the surface features are fully impaled by the fluid and there is no trapped gas.

These experiments were performed using the identical substrates to those described in section 3.1, except the aluminum was anodized with a black dye to allow the gas layer to be viewed. Substrates were wholly submerged in deionized water, to prevent the possibility of atmospheric air replenishing the gas layer. While the beakers in
which the samples were contained were covered to prevent accumulation of debris that might compromise the surfaces, free exchange of gases was allowed with the atmosphere so prevent the creation of an artificial closed environment in the beaker.

<table>
<thead>
<tr>
<th>a) Front View</th>
<th>b) Angled View</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Front View 10 nm surface" /></td>
<td><img src="image2" alt="Angled View 10 nm surface" /></td>
</tr>
<tr>
<td><img src="image3" alt="Front View 250 nm surface" /></td>
<td><img src="image4" alt="Angled View 250 nm surface" /></td>
</tr>
</tbody>
</table>

**Figure 2**: a) Front views of submerged surfaces b) Angled view of submerged surfaces at various points of time following submersion

To verify the presence of the trapped layer of gas (vapor) the property of total internal reflection was used. From the front light passes from the water through the air and is scattered by the substrate on which the spray coating was deposited, in our case a matte black finish (Figure 2a). However when viewed from a position where the incident light is at a high angle, the surface appeared shiny due to reflection at the boundary of the water and gas/vapor (Figure 2b).

The results of the experiment are shown in (Figure 2). From a front view both surfaces appeared matte black at all times in the experiment. When initially submerged, both substrates appeared to have a trapped layer of gas at their surfaces. The layer of gas in the 250 nm surface however appeared to disintegrate very rapidly and was significantly reduced within a few hours (Figure 2b (bottom)). After a duration of 72 hours no presence of the trapped gas could be observed. In comparison the 10 nm surface showed almost no change in the quality of the trapped gas layer over a comparable period of time (Figure 2b (top)). The surface was observed to maintain the gas layer for a period of 127 days. At that point of time it was removed from the beaker and inspected. It was observed that most of the sample was still dry, despite having been immersed in water for a period of over 4 months which suggests the ability of the surface to maintain a layer of gas or vapor over a very long period of time (Figure 3a). The surface was even found to be self-cleaning at that point of time which was demonstrated by using a pipette to place drops of water on the surface held at an angle (Figure 3b).

**3.3. Environmental SEM Condensation Experiments**

The environmental scanning electron microscope (ESEM) provides a unique platform to study superhydrophobic surfaces since it allows the observation of phenomena such as condensation in real time [11, 12]. Using the surfaces...
obtained from the Odom group ESEM condensation experiments were performed. A FEI Quanta sFEG ESEM equipped with a temperature controllable Peltier stage was used to perform the experiments. A drop of water was placed near the stage and allowed to evaporate during pump down of the ESEM to 5 torr, to provide a water vapor rich environment for the sample. The Peltier stage was set to 2°C and the pressure was gradually increased to 6 torr, at which point condensation was observed. While theory predicts that such textured surfaces should resist condensation and require a higher pressure for a particular condition, the change in pressure is too small to be accurately reflected in the ESEM chamber.

3.4. Boiling Experiments
A direct method of measuring increase in heat transfer efficiency, employs the measurement of superheat or heat flux in a boiling setup [13]. We adopted a similar method for studying pool boiling of our superhydrophobic surfaces by mounting them on a hot plate and measuring the superheat required to reach nucleate boiling. While we observed nucleate boiling from the surfaces, it was not possible to make any conclusions regarding the reduction in superheat using textured surfaces. One potential problem is the inability of the hotplate to produce a sufficient heat flux to induce pool boiling.

4. Conclusion
Through the experiments performed we have demonstrated, indirectly, that theory can predict robust surface configurations that would retain their properties even in extreme conditions. Though direct proof of this phenomenon is ideally desirable, the obtained results show a strong correlation with predictions and pave the way for future investigation.

5. References