Micro/Nano Structured Materials for Enhanced
Device Performance and Antibacterial Applications

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Micro/nanostructured materials have been used extensively for various applications due to their unique chemical, physical, and mechanical properties. In this thesis we report the fabrication and characterization of micro/nanostructured materials with antibacterial properties. Plastics are used in a wide range of medical components such as prosthetics, implants, catheters, and syringes. However, contaminating bacteria can attach to plastic surfaces and grow and form biofilms that lead to healthcare associated infections. The consequences on patients and their families are serious, as infections can extend hospital stays, create long-term disability, increase healthcare costs, and even result in unnecessary deaths. Two strategies for creating antibacterial surfaces are (1) anti-biofouling surfaces that make the bacterial attachment process difficult and (2) bactericidal surfaces that kill bacteria cells that come in proximity of or contact the surface. We demonstrate that a fluorine etch chemistry may be utilized to create lotus leaf-inspired, low surface energy, hierarchical micro-structure/nanofibrils in Polypropylene (PP). Our anti-biofouling PP surfaces exhibit a 99.6% reduction of Escherichia coli cell adhesion compared to untreated PP. We also fabricated bactericidal surfaces consisting of uniform and regular nanostructured arrays. The interest in mechanical bactericidal effect has recently increased, as the bacteria cells grow drug resistance. Nanosphere lithography and combination of reactive ion etching and deep reactive ion etching were utilized to prepare these substrates. The pitch, diameter, taper, and height of the nanostructures are controlled. The bactericidal effect of these structures is investigated and significant enhancement in killing is observed.

We also report fabrication of micro/nanostructured materials to improve device performance. Our simulation results show that absorption enhancement in vertical nanowire arrays on a perfectly electric conductor can be further improved through tilting. Tilted
nanowire arrays, with the same amount of material, exhibit improved performance over vertical nanowire arrays over a broad range of tilt angles. The optimum tilt of 53° has an improvement of 8.6% over that of vertical nanowire arrays and 80.4% of the ideal double pass thin film. Incorporation of these structures could improve the efficiency of solar cells.
# Table of Contents

Preface ................................................................. xi

1.0 Introduction ......................................................... 1
  1.1 Types of Micro/Nano Structures ................................. 1
  1.2 Dissertation Outline ............................................ 5

2.0 Tilted Silicon Nanowire Arrays for Photovoltaics ................. 7
  2.1 Introduction ................................................... 7
  2.2 Methods ....................................................... 9
  2.3 Results and Discussion ......................................... 11
  2.4 Conclusion ................................................... 18

3.0 Critical Heat Flux Enhancement in Pool Boiling through Increased
    Rewetting on Nanopillar Array Surfaces .......................... 19
  3.1 Introduction ................................................... 19
  3.2 Methods ................................................................ 21
    3.2.1 Fabrication of Nanopillar Substrates ................. 21
    3.2.2 Boiling Experiment ....................................... 25
    3.2.3 Experimental Validation ................................. 27
  3.3 Results and Discussion ........................................... 29
    3.3.1 Enhancement in Critical Heat Flux and Nucleate Boiling Limit 29
    3.3.2 Mechanism of Heat Transfer Enhancement on Nanopillar Substrates 32
  3.4 Conclusion ....................................................... 36

4.0 Stable Lotus Leaf-Inspired Hierarchical, Fluorinated Polypropylene
    Surfaces for Reduced Bacterial Adhesion ........................... 38
  4.1 Introduction ..................................................... 38
  4.2 Methods ........................................................ 40
    4.2.1 Materials .................................................. 40
    4.2.2 Sample Preparation ....................................... 40
List of Tables

1  Absorption in different spectral regions. ........................................ 16
2  Total solar absorption, short circuit current density, and ultimate efficiency . 16
3  Reactive ion etching parameters .................................................... 22
4  Parameters of fabricated nanopillar substrates. ............................... 22
5  Contact angle and Surface energy of Polypropylene substrates ............. 50
6  XPS surface chemical analysis of the various surfaces ....................... 51
7  Topographical parameters of SiNC substrates .................................. 63
## List of Figures

1. Schematic of the tilted silicon nanowire array structure ........................................ 8
2. Ultimate efficiency of square arrays of vertical nanowires ....................................... 10
3. Ultimate efficiency $\eta$ function of nanowire array tilt angle $\beta$ ........................... 11
4. Absorption as a function of wavelength and nanowire tilt $\beta$ ............................... 13
5. The absorption spectra of the vertical nanowire array ($\beta = 0^\circ$) and worst tilted nanowire array ($\beta = 18^\circ$) ................................................................. 14
6. The absorption spectra of the ideal double pass thin film, vertical nanowire array ($\beta = 0^\circ$), and best tilted nanowire array ($\beta = 53^\circ$) ......................... 15
7. Ultimate efficiency of vertical nanowire and tilted nanowire arrays as a function of incidence angle ................................................................. 17
8. Schematic depiction of the fabrication process ....................................................... 21
9. Nanopillar height vs etch duration during pseudo bosch process ............................ 23
10. SEM images of substrate depicting different steps of fabrication ............................ 24
11. SEM images of fabricated samples ........................................................................ 26
12. Comparison of the boiling curve ............................................................................ 28
13. Representative snapshots showing boiling phenomenon on the smooth substrate and nanostructured substrate ................................................................. 30
14. (a) Heat flux versus wall superheat for smooth and nanopillar substrates. (b) Dependence of critical heat flux, CHF temperature, and Leidenfrost temperature on surface roughness ................................................................. 33
15. (a) Schematics showing that the rewetting process in pool boiling is similar to the spreading process, (b) Apparent spreading velocity of FC-72 on different substrates, (c) Prediction of critical heat flux .................................................. 34
16. Top view SEM images of different PP samples ....................................................... 44
17. Tilted view SEM images of different PP samples .................................................. 45
18 (a) AFM characterization, (b) Power spectral density as a function of roughness wavelength...
19 Contact angle of different samples and representative images...
20 Contact angle hysteresis of different samples...
21 Water contact angle of different samples over time...
22 XPS survey scan of control sample...
23 XPS survey scan of LP Oxygen treated sample...
24 XPS survey scan of HP Oxygen treated sample...
25 XPS survey scan of Fluorinated sample...
26 Comparison of XPS survey scan of fresh fluorinated samples and 1-week old fluorinated samples...
27 Bacterial counts per mm² for different samples and fluorescent images of PP samples with adhered bacteria...
28 SEM image of fabricated SiNC substrates. a) Bare silicon, b) 1400 nm pitch, c) 800 nm pitch, d) 500 nm pitch, e) 300 nm pitch.
29 Measured water contact angle of fabricated bactericidal samples. Error bars indicate standard error.
30 Representative optical images of plates of the 0 hour time point at the end of the 24 hour incubation period.
31 Representative optical images of plates of the 3 hour time point after the 24 hour incubation period. (a) bare silicon, (b) 1400 nm, (c) 800 nm, (d) 500 nm, (e) 300 nm pitch samples.
32 Percentage of dead cells after 3 hour incubation of S. epidermidis on fabricated bacteridial samples. Error bars indicate standard error.
33 SEM image of punctured bacteria cell on 300 nm pitch samples. (a,b) top view, (c) tilted view.
34 Tilted view SEM image of bacteria cell on different samples. (a,b) 500 nm, (c) 800 nm, (d) 1400 nm pitch samples.
35 Ultimate efficiency of square arrays of vertical nanowires of height 500 nm...
Preface

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1.0 Introduction

Micro/nano structured materials have been studied extensively in the recent years and the use of these materials have increased drastically over the years. These materials have their unique chemical, physical, and mechanical advantages and have vast application in various research fields. Micro/nanostructured materials have been used for electronic devices, sensors, water treatment, automotive, aerospace engineering, communication engineering, medicine, and antibacterial applications [1]. Nanotubes, polymeric nanofibers, nanoparticles, nanowires, nanocomposites, and micropillars are some of the commonly reported micro/nanostructures that have been used for the above-mentioned applications.

1.1 Types of Micro/Nano Structures

Nanotubes

Nanotubes are hollow tube-like structures, generally having diameter in the nanoscale, while the length ranges from nanoscale to microscale [2]. Based on the number of layers of atoms wrapped around the hollow core nanotubes can be categorized as single walled or multi walled. Nanotubes made of different materials such as Carbon, Boron Nitride, Titania, Silica, Silicon etc have been fabricated [3, 4, 5, 6, 7, 8]. Among these Carbon nanotubes (CNTs) have been studied extensively and used for various applications such as energy storage materials, gas storage materials, polymer reinforcements, electronics, field emission displays and radiation sources; semiconductor devices, probes, interconnects and biosensors [9, 10, 11]. The combination of superior thermal, mechanical and electronic properties of CNTs have made them useful for different application [12]. Titania nanotubes have also shown enhanced properties for application in sensing, photoelectrolysis, photocatalysis, and photovoltaics [13].
Nanoparticles

Nanoparticles (NPs) are microscopic particles having a size between 1-100 nm. NPs being cheap, easy, and reproducible have been used for electronic, optoelectronic, and photoelectronic applications [14, 15, 16]. Novel applications such as cleaning up pollutants in water and leaving only biodegradable compounds have also been reported [17]. NPs have been used in the biological field extensively due to having important properties such as fluorescence and magnetic behavior [18]. The size of NPs being comparable to biomolecules such as proteins also play an important role. Silver NPs have found considerable usage in the biomedical field, while their plasmonic-resonance optical scattering property have enabled them to be used for bio-sensing and imaging applications [19]. Gold NPs have been used to develop colorimetric biosensors due to their size dependent optical and chemical properties [20]. They have also been used in drug delivery applications, as the gold core is inert and non-toxic [21].

Nanofibers

Nanofibers (NFs) have found considerable interest due to the advantages they offer. They are lightweight, have high surface area to volume ratio have small diameters and have controllable pore structures [22, 23]. NFs have been used for chemical, biological, and optical sensors, as well as for biomedical applications such as tissue engineering and drug delivery [24]. NFs have also been used for piezoelectric polymeric nanogenerators capable to convert mechanical energy to electricity [25]. Electrospun polymeric NFs have been used for wound dressing as they support cell adhesion, migration, growth which are important for the wound healing process [26]. Carbon NFs have been used to remove cationic pollutants, to develop supercapacitors, and as an electrode for vanadium redox flow battery [27, 28, 29, 30].
Nanowires

Silicon nanostructures have been subjected to comprehensive studies to evaluate their significant impact on electronic devices. Due to their unique electrical, optical, and structural properties these nanostructured surfaces have been used for various applications. Silicon nanowires (SiNWs) have been used for various applications such as photovoltaics [31, 32], chemical and biological sensors [33, 34, 35, 36, 37, 38], field effect transistors [39] etc. Similarly silicon nanocone (SiNC) arrays have been used for self-cleaning antireflection coatings [40], solar cells [41], fuel cells [42, 43], improved lithium-ion batteries [44] etc. The use of nanostructured surfaces is not limited to these scopes only. They have also been used for antibacterial biomedical devices [45, 46]. Nanowire structures have been used in solar cells as they provide several advantages such as reduced reflection, improved band gap tuning, extreme light trapping, increased defect tolerance, enhanced charge transport capacity [47, 48]. This results in significant cost reductions as reduced amount of materials are used. Nanowires have also been used for highly transparent flexible metal electrode touch panel, high performance anode for lithium ion batteries, gas sensors, supercapacitors, fully stretchable light-emitting diodes etc [49, 50, 51, 52, 53].

Nanocomposites

Nanocomposites (NCs) can be regarded as multiphase nanostructures with one phase being at the nanoscale dimension [23]. Continuously fabricated transparent conductive polycarbonate/carbon nanotube NC films have been used for switchable thermochromic applications [54]. These transparent conductors have shown excellent mechanical flexibility, and good environmental resistance. NC hydrogels have also been used for environmental protection applications such as ion exchangers, adsorption, photocatalysis and soil conditioning and biomedical engineering applications such as drug delivery agents, wound dressing, and tissue engineering [55]. Graphene based NC fibers have shown antibacterial property, low cytotoxicity, and ultrahigh ultimate tensile strength [56]. Different NC materials also have been used for antibacterial applications [57, 58, 59, 60].
Micropillars

Micropillars (MPs) have been used to study boiling heat transfer and critical heat flux extensively [61, 62, 63]. Boiling heat transfer on MP substrate was reported to increase with the surface roughness ratio [64]. MP structured surfaces have been used to study wetting behaviors and transition from the Cassie-Baxter state to the Wenzel state [65]. MP arrays have been used for optoelectronic applications [66, 67]. Incorporation of tilted MPs also enhanced the performance of flexible capacitive Pressure sensors [68]. MPs have also been used for solar cells and showed improved efficiency [69, 70]. MPs have been used as an anti reflection coating for solar cells and shown stretchability without affecting the device functionality [71, 72].
1.2 Dissertation Outline

The research focus of this dissertation is divided into two parts. In the first part we evaluate the use of silicon nanostructures to improve device performance. In our first study, we did Finite-Difference Time-Domain (FDTD) simulation to evaluate the optical performance of tilted Silicon nanowire array. Silicon nanowire arrays have been shown to demonstrate light trapping properties and promising potential for next-generation photovoltaics. In this study, we performed systematic and detailed simulation studies on the optical properties of tilted silicon nanowire arrays as compared to vertical nanowires arrays. Our results show that the absorption enhancement in vertical nanowire arrays on a perfectly electric conductor can be further improved through tilting. Tilted nanowire arrays exhibit improved absorption over the solar spectrum compared with vertical nanowires since the tilt removes symmetry requirements on the resonance modes in the nanowires. The results were published in [73].

Then we did experimental and theoretical analysis to control critical heat flux and boiling crisis using Silicon nanopillars. Boiling is a key heat transfer process for a variety of power generation and electronics cooling technologies. In such applications, it is very important to improve the energy efficiency by increasing the critical heat flux (CHF), and to reduce the operational risks by avoiding the boiling crisis. In this study, we show that nanopillar arrays fabricated on a substrate enhance both the critical heat flux (CHF) and the critical temperature at CHF of the substrate and thus, effectively increase the limit of boiling before the boiling crisis is triggered. We conclude that the enhancement in both the CHF and the critical temperature results from an intensified rewetting process which increases with the height of nanopillars. The results were published in [74].

Infections due to bacterial adhesion is very common for implanted medical devices and extensive research is being done to address this issue. In the second part of the thesis we evaluate the adhesion and killing of bacteria cells by antibacterial surfaces. First we report on the micro/nanostructuring and surface functionalization of Polypropylene (PP) substrate, which is used in a wide variety of medical components, through various oxygen and fluorine reactive ion etching (RIE) treatments and their effects on wettability and bacteria adhesion. The results were published in [75].
The interest in mechanical bactericidal effect has increased, as the bacteria cells grow drug resistance. We fabricated uniform and regular nanostructured arrays with control over pitch, diameter, taper, and height. Nanosphere lithography and combination of reactive ion etching and deep reactive ion etching were utilized to prepare uniform silicon nanostructure arrays of different morphology. The bactericidal effect of these structures were investigated against Gram-positive bacteria (*Staphylococcus epidermidis*). Gram-positive bacteria have a thicker cell wall compared to Gram-negative bacteria, and has been reported difficult to kill mechanically. Our results shows that the center-to-center spacing among the pillars plays an important role in the bactericidal performance of the substrate. Significant enhancement in killing (82%) was observed for 1 µm long, 300 nm pitch nanostructured surface with a tip diameter of 80 nm compared to the flat control substrates.
2.0 Tilted Silicon Nanowire Arrays for Photovoltaics

2.1 Introduction

Silicon is a naturally abundant, stable, non-toxic material that has been used extensively for semiconductor devices so that its processing and manufacturing is well developed. While silicon has an almost-ideal band gap for single p-n junction photovoltaics, its infrared absorption is poor. Typical single-crystalline silicon photovoltaics are thus usually several hundred microns thick to absorb sunlight effectively. These silicon solar cells require costly manufacturing processes such as purification, crystallization, and wafer slicing in order to ensure that generated carriers are collected efficiently. Light trapping helps address this issue by increasing the distance photons travel in the silicon before escaping to increase absorption and efficiencies for a particular active layer thickness. Manufacturing costs are reduced because less silicon and poorer quality silicon may be used. Poorer quality silicon with smaller minority carrier diffusion lengths may be used because charge carriers have to diffuse over smaller distances in order to be collected. A variety of structures have been investigated for utilizing light trapping to increase absorption in thin film silicon photovoltaics such as diffraction gratings [76], grating couplers [77], photonic crystals [78, 79, 80, 81], and random surface textures [82, 83]. These structures contain features that are the same size or smaller than the wavelength of light, such that conventional geometrical light trapping limits (the Yablonovitch or Lambertian limit [84, 85]) are no longer applicable. Much solar cell research has focused on silicon (Si) nanowires, which have been demonstrated to be a promising active layer material for next-generation solar cells [86, 87, 88, 89, 90, 91, 92, 93, 94, 95]. Nanowires may orthogonalize light absorption and carrier collection processes to facilitate high optical absorption and efficient collection of photogenerated carriers [96]. Furthermore, nanowires have demonstrated light-trapping properties, where their absorption is enhanced over that of planar silicon [88, 86, 87, 94]. These structures may also be deposited on low-cost or flexible substrates using chemical vapor deposition or contact transfer methods [97]. Various
structures that break the symmetry of nanowire arrays such as nanocones [98, 99, 100] or aperiodic vertical arrays [101] have been demonstrated to have increased absorption over vertical nanowire arrays.

![Schematic of the tilted silicon nanowire array structure.](image)

Figure 1: Schematic of the tilted silicon nanowire array structure. The nanowires sit on a perfectly electric conductor and are defined by the height $h$, circular cross-sectional diameter $d$, and tilt with respect to the zenith $\beta$. The nanowires form a two-dimensional lattice defined by the lattice vectors $\vec{a}_1$ and $\vec{a}_2$, where $|\vec{a}_2| = a$ and $|\vec{a}_1| = a / \cos \alpha$. The incidence angle of the incoming radiation is defined with respect to the negative z-direction.

In this study, we investigate the optical performance of tilted nanowire arrays on a metal contact and compare their performance to that of vertical nanowire arrays. We report how the nanowire tilt may be used to improve solar absorption and thus, ultimate efficiency. We demonstrate that this enhancement occurs over a broad range of incidence angles.
2.2 Methods

Figure 1 shows a schematic of the tilted silicon nanowire arrays studied, which sit on top of a perfectly electric conductor (PEC). The PEC may be, for example, the idealized perfectly reflecting back contact of a solar cell. The parameters of the structure are the height $h$, circular cross-sectional diameter $d$, and tilt with respect to the zenith $\beta$. The nanowires form a two-dimensional lattice defined by the lattice vectors $\vec{a}_1$ and $\vec{a}_2$ where $\vec{a}_1$ and $\vec{a}_2$ are in the $x$- and $y$-directions respectively. The nanowires are tilted in the $x$-$z$ plane. $|\vec{a}_2| = a$ and $|\vec{a}_1| = a/\cos \beta$, where $a$ is the vertical nanowire pitch. The total nanowire array volume is invariant with $\beta$ since the fill factor $(\frac{\pi d^2}{4a^2})$ is independent of $\beta$. $d \leq a$ in order to avoid the intersection of nanowires. We studied nanowires with $h = 1000$ nm.

Maxwell’s equations were solved using the finite difference time domain (FDTD) method, which computes the energy dependent transmission $T(E)$, reflection $R(E)$, and absorption spectra $A(E)$ efficiently. The ultimate efficiency is calculated using the following equation

$$\eta = \frac{\int_{E_g}^{\infty} I(E)A(E)\frac{E_g}{E}dE}{\int_{0}^{\infty} I(E)dE}$$  \hspace{1cm} (2.1)$$

where $E$ is the photon energy, $E_g$ is the band gap of crystalline silicon, $I(E)$ is the solar irradiance under the global 37° tilt Air Mass 1.5 spectrum [102], and $A(E)$ is the absorption [103]. The ultimate efficiency is the maximum efficiency of a solar cell when the temperature approaches 0 K, where there is no recombination and each absorbed photon produces an electron-hole pair. The band gap $E_g = 1.12$ eV for crystalline silicon. The absorption and reflection spectra was obtained over the energy range of the solar spectrum from $E = 1.12$ to 4.13 eV (wavelengths from 1100 to 300 nm). Assuming each photon produces an electron-hole pair and there is no recombination, such that all photogenerated carriers are collected, the short circuit current density is

$$J_{sc} = q \int_{E_g}^{\infty} b_s(E)A(E)dE$$  \hspace{1cm} (2.2)$$
where $q$ is the elementary charge and $b_s(E)$ is the photon flux density. The irradiance and photon flux density are related by $I(E) = E b_s(E)$. The total solar absorption is calculated from

$$A_{\text{sol}} = \frac{\int_{E_g}^{\infty} b_s(E) A(E) dE}{\int_{0}^{\infty} b_s(E) dE}. \quad (2.3)$$

The optical constants for silicon were taken from experimental measurement results in Palik’s *Handbook of Optical Constants of Solids* [104]. A non-uniform mesh with a minimum size of 15 nm was used for the simulation. Perfectly matched layer boundary conditions were used for the upper boundary of the simulation cell [105], PEC boundary conditions were used for the lower boundary of the simulation cell, while appropriate boundary conditions were used for the side boundaries to model the periodic nature of the arrays.

Figure 2: Ultimate efficiency of square arrays of vertical nanowires. The vertical nanowires ($\alpha = 0$) have height $h = 1000$ nm and the ultimate efficiency is shown as a function of array pitch $a$ and nanowire diameter $d$. The highest ultimate efficiency is 29.7% at $a = 600$ nm, $d = 560$ nm, which is marked with a circle in the contour plot.
2.3 Results and Discussion

We first focused on evaluating vertical nanowires where $\beta = 0$. The vertical nanowires form a square lattice where $|\vec{a}_1| = |\vec{a}_2| = a$. $h = 1000$ nm as mentioned before. We varied the pitch $a$ from 40 nm to 1000 nm and the diameter from 20 nm up to the pitch. Figure 2 shows the results of our studies. The best vertical nanowire array was determined to be with $a = 600$ nm and $d = 560$ nm, which is marked with a circle in the contour plot. The pitch of 600 nm is the same as that found in previous research [87, 106]. High efficiencies are generally achievable from arrays with high fill factors. The best vertical nanowire has an ultimate efficiency of 29.7%.

![Figure 3: Tilted nanowire array simulation results. Ultimate efficiency $\eta$ function of nanowire array tilt angle $\beta$. The short circuit current density is shown on the right y-axis. The nanowires have height $h = 1000$ nm, diameter $d = 560$ nm, and vertical pitch $a = 600$ nm.](image-url)
The vertical nanowire array with \( a = 600 \text{ nm} \) and \( d = 560 \text{ nm} \) has the same amount of silicon as a flat thin film structure with a thickness of \( L = 684 \text{ nm} \). For comparison purposes, we compare the performance of double pass thin films. The double pass thin film assumes perfect antireflection at the front surface of the thin film and perfect reflection at the back surface, such that light passes through the material twice with no light trapping. The absorption for double pass thin films under normal incidence light is

\[
A(E) = 1 - \exp[-2\alpha(E)L]
\]

where \( \alpha(E) \) is the energy dependent absorption coefficient of Si. The ultimate efficiency of an ideal double pass thin film with \( L = 684 \text{ nm} \) is 17.9\%. We also studied the similar properties of the 500nm nanowires. The highest efficiency was obtained for 680 nm pitch and 640 nm diameter, which is shown in Appendix A.

Next, we studied tilted nanowire arrays. The pitch and diameter were fixed at \( a = 600 \) and \( d = 560 \text{ nm} \) respectively, while the nanowires were systematically tilted by varying \( \beta \). The height is \( h = 1000 \text{ nm} \) as before. As mentioned earlier, the amount of silicon does not change as the wires are tilted. Simulation were performed with the normal incident light polarized in the \( x \)-direction and then, in the \( y \)-direction as the nanowires are tilted. Results of our tilted nanowire array studies are plotted. Figure 3 plots the ultimate efficiency \( \eta \) as a function of the nanowire array tilt angle \( \beta \). \( \eta = 29.7\% \) for the vertical nanowire array (\( \beta = 0^\circ \)). A horizontal dash-dotted line is shown at this ultimate efficiency for references. The ultimate efficiency is shown for incident light polarized in the \( x \)-direction, \( y \)-direction, and the average of these two results.

By tilting the nanowires, higher average ultimate efficiencies may be achieved at nanowire array tilts between 38 and 72\°. The ultimate efficiency is 32.2\% and a maximum at \( \beta = 53^\circ \), which is indicated with a vertical dotted line. \( a_1 = 997 \text{ nm} \) at this tilt. Figure 4 plots the absorption as a function of the wavelength and nanowire tilt angle \( \beta \). The absorption shown is the average of the two polarizations. The optimum tilt of \( \beta = 53^\circ \) is again marked with a dashed line in the contour plot. Normal incident light can only couple to \( \text{HE}_{1m} \) in vertical nanowires due to symmetry requirements [107]. Distinct resonance peaks can be seen in the absorption spectrum of the vertical nanowire array. For tilts less than 38\°, the ultimate
efficiency decreases when compared to the vertical nanowire arrays. The minimum ultimate efficiency is 24.0% at $\beta = 18^\circ$. Figure 5 plots the absorption spectra of the vertical nanowire array ($\beta = 0^\circ$) and this tilted nanowire array. The absorption spectra of the $\beta = 18^\circ$ tilted nanowire array closely resembles that of the vertical nanowire array, but the magnitude of the various absorption resonances are lower. For small tilt angles, the ultimate efficiency decreases because the excitation efficiencies of the $\text{HE}_{1m}$ modes decrease. However, as the nanowire is tilted, additional modes besides the $\text{HE}_{1m}$ modes may be excited. The overall absorption for tilted nanowires is thus increased compared to tilted nanowires for higher tilt angles. The tilted nanowires exhibit improved performance over vertical nanowires over the range of $\beta = 38$ to $72^\circ$.

Figure 6 plots the absorption spectra of the ideal double pass thin film, vertical nanowire array, and best tilted nanowire array. Table 1 lists the fraction of photons absorbed in different regions of the solar spectrum for these three. The infrared region (above the Si
Figure 5: Tilted nanowire array simulation results. The absorption spectra of the vertical nanowire array ($\beta = 0^\circ$) and worst tilted nanowire array ($\beta = 18^\circ$).

The absorption band gap is from 1.12 to 1.67 eV (1100 to 740 nm), the visible region is from 1.67 to 3.1 eV (740 to 400 nm), and the ultraviolet region is from 3.1 to 4.4 eV (400 to 280 nm). The total absorption shown only includes the range above the c-Si band gap energy from 1.12 to 4.4 eV (1100 to 280 nm). Vertical nanowire arrays have improved absorption in the lower energy regime (infrared and visible region) compared with the ideal double pass silicon thin film due to light trapping. Tilted nanowire arrays improve the light trapping performance even more by increasing absorption across the infrared, visible, and ultraviolet regions compared to the vertical nanowire arrays.

The performance of these three different structures for solar cells are compared in Table 2. The total solar absorption, ultimate efficiency, and short circuit current density are all shown in this Table. The total solar absorption shown in this table is over the entire solar spectrum and not just over energies above the silicon band gap as shown in Table 1. The ultimate efficiency of the vertical nanowire arrays is 29.7%, a 66.2% improvement over the 17.9% exhibited by the ideal double pass thin film with the equivalent amount of material.
The absorption spectra of the ideal double pass thin film, vertical nanowire array ($\beta = 0^\circ$), and best tilted nanowire array ($\beta = 53^\circ$).

The ultimate efficiency of the tilted nanowires arrays is 32.2%, or an improvement of 8.6% compared to vertical nanowire arrays or 80.4% over the ideal double pass thin film. These simulations demonstrate the potential of tilted nanowire arrays to improve the performance of vertical nanowire arrays under normal incidence.

We further studied the performance of the nanowire arrays under oblique incidence. The source was varied from $\theta = -90^\circ$ to $90^\circ$ for the best vertical nanowire array ($a = 600$ nm, $d = 560$ nm, and $\beta = 0^\circ$) and the best tilted nanowire array ($a = 600$ nm, $d = 560$ nm, and $\beta = 53^\circ$). The incidence angle $\theta$ is with respect to the negative $z$ direction as shown in the Figure 1 schematic. Figure 7 shows results for transverse electric (TE) waves, which are linearly polarized transverse to the plane of incidence, and transverse magnetic (TM) waves, which have linear polarization so that the magnetic field is purely transverse. Our results at an incidence angle of $\theta = 0^\circ$ are slightly different from that above due to the use of different boundary conditions. The performance of the vertical nanowire arrays is symmetric.
Table 1: Absorption (%) in different spectral regions. The infrared and total solar regions are calculated for those portions that are above the Si band gap ($E > 1.12$ eV).

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>IR</th>
<th>Vis</th>
<th>UV</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Double Pass</td>
<td>6.0</td>
<td>59.4</td>
<td>100.0</td>
<td>36.4</td>
</tr>
<tr>
<td>Vertical Nanowire Array</td>
<td>41.8</td>
<td>70.5</td>
<td>57.2</td>
<td>60.5</td>
</tr>
<tr>
<td>Tilted Nanowire Array</td>
<td>46.7</td>
<td>74.7</td>
<td>60.0</td>
<td>65.7</td>
</tr>
</tbody>
</table>

Table 2: The total solar absorption, $A_{sol}$ (%), short circuit current density $J_{sc}$ (mA/cm$^2$), and the ultimate efficiency $\eta$ (%).

<table>
<thead>
<tr>
<th></th>
<th>$A_{sol}$</th>
<th>$J_{sc}$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Double Pass</td>
<td>23.1</td>
<td>15.9</td>
<td>17.9</td>
</tr>
<tr>
<td>Vertical Nanowire Array</td>
<td>38.4</td>
<td>26.5</td>
<td>29.7</td>
</tr>
<tr>
<td>Tilted Nanowire Array</td>
<td>41.7</td>
<td>28.8</td>
<td>32.2</td>
</tr>
</tbody>
</table>
with respect to positive and negative incidence angles. While freestanding vertical nanowire arrays have better performance under TM-polarized incident light than TE [93, 87], our results indicate that vertical nanowire arrays on a perfect back reflector have the opposite trend where the ultimate efficiency is higher for TE polarization than TM polarization. The increased absorption under TM-polarized incident light in freestanding vertical nanowires is due to reduced transmission [108], whereas our system has no transmission due to the perfect back reflector.

Figure 7: Ultimate efficiency of vertical nanowire and tilted nanowire arrays as a function of incidence angle $\theta$. The TE polarization results for the tilted nanowire arrays are the average of the light polarized along the x-axis and the y-axis. Likewise, the TM polarization results for the tilted nanowire arrays are the average of the magnetic field along the x-axis and the y-axis. The tilted nanowire arrays consistently perform better than the vertical nanowire arrays for incidence angles under about 60°.
In our simulations of tilted nanowires, the performance is symmetric with respect to positive and negative incidence angles for TE waves with electric field along the x-axis and TM waves with magnetic field along the y-axis. However, this symmetry is broken for TE-incidence with electric field along the y-axis and TM-incidence with magnetic field along the x-axis. The results shown for the tilted nanowire arrays are the average of the two orthogonal polarizations. The performance of the tilted nanowires is slightly better under positive incidence angles versus negative incidence angles, where the Poynting vector is closer to along the axis of the nanowire. In addition, we note that the performance of the tilted nanowires is consistently higher than that of the vertical nanowire arrays for incidence angles under about 60°. For high angles of incidence, the performance of the vertical and tilted nanowires converge for both TE-incidence and TM-incidence.

2.4 Conclusion

We have performed a comparative study of the optical performances of tilted silicon nanowire arrays on a perfectly electric conductor for photovoltaic applications using the finite difference time domain method. Our results show that the absorption enhancement in vertical nanowire arrays over silicon thin films can be further improved through tilted nanowires. Optimized vertical nanowire arrays with a height of 1000 nm have a 66.2% ultimate efficiency improvement over an ideal double pass thin film of the equivalent amount of material. Tilted nanowire arrays, with the same amount of material, exhibit improved performance over vertical nanowire arrays over a broad range of tilt angles (from 38 to 72°). The optimum tilt of 53° has an improvement of 8.6% over that of the vertical nanowire arrays and 80.4% of the ideal double pass thin film. Tilted nanowire arrays exhibit improved absorption over the infrared, visible, and ultraviolet regime compared with vertical nanowires since the tilt removes symmetry requirements on the resonance modes in the nanowires. We also observed that tilted nanowire arrays have improved performance over vertical nanowire array over a large range of incidence angles (under about 60°).
3.0 Critical Heat Flux Enhancement in Pool Boiling through Increased
Rewetting on Nanopillar Array Surfaces

3.1 Introduction

Boiling is a central phenomenon in technological and industrial applications as diverse as thermal management in electronics, power generation and chemical processing [109, 110, 111]. Pool boiling is the process, when a stagnant pool of liquid is heated and boiling occurs in the liquid at the bottom of the bulk liquid pool. Four different regimes can be seen in the pool boiling curve: natural convection, nucleate boiling, transition boiling, and film boiling. Nucleate boiling regime is important, as high heat flux can be achieved without damaging the substrate. The enhancement of the energy efficiency during boiling applications can be done by increasing the critical heat flux (CHF), the highest heat flux a boiling substrate can achieve. Increasing the CHF also reduces the operational risks by avoiding the notorious “boiling crisis,” a major cause of burnouts in boilers or heat exchanging devices [112]. The boiling crisis occurs because of excessive vaporisation of liquid on a boiling substrate. A vapor layer is formed which severely impedes heat transfer through the substrate and a sudden jump in the surface temperature is observed. Subsequently the substrate of the boiling equipment is damaged irreversibly. The temperature $T_c$ at which CHF occurs, known as the critical temperature, therefore is directly connected to the boiling crisis; a boiling system operating at temperature higher than $T_c$ inevitably drifts towards the boiling crisis. In order to enhance the boiling performance and to avoid the boiling crisis both CHF and critical temperature $T_c$ need to be increased.

Many studies have been conducted to understand the mechanism of nucleate boiling. With increasing surface temperature, CHF is the upper bound of heat flux in the nucleate boiling regime before the boiling crisis occurs [113]. Different microscale models have been proposed to explain nucleate boiling heat transfer mechanisms [114]. Latent heat transfer is dominant compared to convective heat transfer in the nucleate boiling regime. Surface roughness ranging from nano- to micro-scales [115], and wettability [116] have been reported
as important parameters which affect the heat flux in the nucleate boiling regime. To increase the critical heat flux researchers have followed two major approaches: fluid modification and surface treatment. However, fluid modification approach uses additives [117, 118] or nanoparticles [119] and puts constraints on fluid selection and operating conditions of the boiling system [120]. The surface treatment approach includes either treatments to enhance surface wettability [121, 122], or morphological alteration of the substrate. Incorporation of porous coatings [123, 124], artificial fins [125, 126, 127] and nano/microstructures [120, 128] are some of the examples of morphological alteration. Although numerous surface modification methods have been found to increase CHF, in particular those utilising nano/microstructures, the roles of surface structures at different length scales in changing the heat flux and the critical temperature remain elusive. Although it has been suggested that nanoscale structures may intensify the wetting velocity, which is a crucial factor leading to CHF enhancement [122, 129], the relation between a systematic change in nanoscale structures, wetting velocity and CHF has not been established. Moreover, little effort has been made to relate surface wettability or nanoscale structures to the change in the critical temperature $T_c$.

In this study, we investigate the boiling phenomenon of FC-72 on nanostructured surfaces. Fluorinert liquid FC-72 is an ideal coolant liquid commonly used in various heat management applications and has a low boiling point (56°C). We show that modifying the surface morphology at nanoscales leads to significant enhancement in the boiling performance, including both the critical heat flux and the critical temperature. By using nanopillars with systematically varying heights on silicon substrates, we demonstrate scalable boiling enhancement with increasing height of nanopillars. The enhancement in both the CHF and the critical temperature results from an intensified rewetting process which increases with the height of nanopillars.
3.2 Methods

3.2.1 Fabrication of Nanopillar Substrates.

The nanopillar silicon substrates are obtained by Inductively Coupled Plasma Reactive Ion Etching (ICPRIE). The process flow is shown in Figure 8. The fabrication process consists of three steps, (1) manufacture of the etching mask, (2) etching the underlying silicon by ICPRIE, and (3) removal of etching mask. Polystyrene (PS) nanospheres are utilised to generate the etching mask.

First, a monolayer of nanospheres with the diameter of 800 nm are self-assembled in the air-water interface [130, 131, 132]. Subsequently the monolayer is transferred to a P-type boron-doped (100) silicon substrate, which has been cleaned with acetone, methanol, isopropanol and then dried with nitrogen gas. After the substrate is dried in air at room temperature, Reactive Ion Etching (RIE) with oxygen is applied to reduce the diameter of nanospheres to the required size (≈440 nm). During the RIE process the pressure was set at 25 mTorr and the RF power was set at 25 W. The flow rate of oxygen was 25 sccm, which yielded an etch rate of 80 nm per minute. The duration of the RIE process was 270 seconds. By varying the RIE duration, it is possible to vary the diameters of the mask and hence that of the nanowires.

![Figure 8: Schematic depiction of the fabrication process.](image-url)
Table 3: Reactive ion etching parameters

<table>
<thead>
<tr>
<th>Gas</th>
<th>Flow Rate (sccm)</th>
<th>Pressure (mTorr)</th>
<th>Power (Watts)</th>
<th>Duration (mintues)</th>
<th>Etch Rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>variable</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 4: Parameters of fabricated nanopillar substrates.

<table>
<thead>
<tr>
<th>Etch duration (minute)</th>
<th>Top radius $d_t$ (nm)</th>
<th>Bottom radius $d_b$ (nm)</th>
<th>Height $h$ (nm)</th>
<th>Roughness $r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>440</td>
<td>440</td>
<td>260</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>440</td>
<td>440</td>
<td>390</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>440</td>
<td>440</td>
<td>690</td>
<td>2</td>
</tr>
<tr>
<td>6.5</td>
<td>200</td>
<td>405</td>
<td>1390</td>
<td>3.2</td>
</tr>
</tbody>
</table>
After the etching mask is manufactured, ICPRIE is used to etch the silicon substrate to fabricate silicon nanopillars with desired dimensions. Mixed mode of operation is used to fabricate the samples instead of the commonly used Bosch process. The difference between the mixed mode and the Bosch process is that during the Bosch process there are two different steps that work during each cycle. First the etching gas is flown and then the passivation gas is flown. The gases are flown separately. The purpose of using the passivation gas is to make the sidewalls smooth. However, due to the separation of etching and passivation step the nanowires has the spiral structures. The number of cycles of these steps determine the length of the nanowires. On the other hand during the mixed mode process, which has also been referred as the pseudo Bosch etching method, both the passivation and etching gases are flown together. The etch rate is comparatively slower than the Bosch process, but the vertical sidewalls of the nanowires are smooth and the spiral structures are avoided. SF$_6$ is used for etching purpose and C$_4$F$_8$ is used for passivation purpose. The ratio of the etch and passivation gas is varied to find the optimized ratio for fabricating silicon nanopillars.
Figure 10: SEM images of Silicon substrate a) After Nanosphere Lithography, b) after Reactive Ion Etching, c) after Deep Reactive Ion Etching and ultrasonication.
Three different gas ratios were used to evaluate the fabricated nanopillars, while other process parameters were kept constant. Ratio of SF$_6$ and C$_4$F$_8$ was 33:57, 33:82, 33:110 for three different batches of samples. Based on the SEM images of these samples, the optimal ratio of SF$_6$ and C$_4$F$_8$ is found to be 33:82 and is used for subsequent runs. Different height of nanopillars are obtained by varying the duration of this step. The ICP power, and forward power were 600 Watts and 20 Watts respectively.

It should be noted that when the time duration is longer than 5 minutes the PS mask is impacted and the nanopillar base diameter is different from the etching mask. When the etching is completed, the PS mask is be removed by ultrasonication in acetone for 5 minutes.

### 3.2.2 Boiling Experiment.

Initially, fabricated silicon nanopillar substrates were sent to our collaborators at the Nanyang Technological University, Singapore for boiling experiments. Based on their feedback a second batch of samples with optimized parameters were prepared and sent to them again. Details of those samples were provided in the previous section and those samples were used for the boiling experiments. The experimental setup used to measure the heat flux through different substrates consisted of three sections: heating, testing and condensation. In the heating section, a cartridge heater embedded in a cylindrical copper rod was used to generate heat. A Teflon holder was used to insulate the copper rod from the surrounding environment. In the testing section, a boiling substrate is placed between the copper rod and a glass cuvette. The test substrate was cleaned with organics (ethanol and acetone) in a ultrasonic bath and rinsed with distilled water before each experiment. The cuvette was filled with degassed FC-72 as a working liquid and was enclosed by a stainless steel container. Hot water of temperature 55.5±0.5°C was circulated in the gap between the cuvette and the container to keep the temperature of the working liquid close to the boiling point. Two glass windows on two opposite sides of the container enabled the optical recording during the boiling experiment. A condenser was used to collect vapor generated from the working liquid. The cooling power of the condenser was adjusted to keep the vapor pressure inside the cuvette at atmospheric pressure.
Figure 11: SEM images of fabricated samples and corresponding surface roughnesses $r$. 

![SEM images of fabricated samples](image-url)
The vapor pressure was measured by pressure transducer (Gefran) and maintained at atmospheric pressure by adjusting the cooling power of a Peltier module. The temperature was measured by K-type thermocouples and the boiling process was recorded by a high speed camera (SA-5, Photon). Three thermocouples were distributed along the asymmetrical axis of the copper cylinder. The temperatures measured by these thermocouples were used to calculate the heat flux \( q \) through the test substrate and the surface temperature \( T \). The heat flux in the vertical direction was approximated with the assumption that the rate of heat loss to the side was constant \[133, 134\]. Thus the heat flux through the substrate was estimated as:

\[
q = 0.5k_c (4T_2 - T_1 - 3T_3) \Delta x_c^{-1}.
\]

where \( k_c \) was the thermal conductivity of copper, \( T_1, T_2, T_3 \) were obtained from the thermocouples in the copper rod, and \( \Delta x_c \) was the distance between them. There were three layers between the top thermocouple and the top surface: a copper layer (7 mm), a thermal glue layer (\( \approx 10 \mu m \)) and the silicon substrate (500 \( \mu m \)). The surface temperature \( T \) of the test substrate was then estimated by the one-dimensional heat conduction equation:

\[
T = T_3 - q \left( \Delta x_c k_c^{-1} + \Delta x_g k_g^{-1} + \Delta x_s k_s^{-1} \right),
\]

where \( \Delta x_c/k_c, \Delta x_g/k_g \) and \( \Delta x_s/k_s \) denoted the heat resistance of copper, thermal glue, and silicon substrate respectively. For each tested substrate, the heat flux \( q \) and the corresponding superheat \( \Delta T = T - T_b \) were measured when the system was in the steady state and with temperature steps of 5 K. The experimental uncertainty was obtained by repeating the experiment three times.

### 3.2.3 Experimental Validation.

The measurement procedure and analysis were validated by comparing the heat transfer data obtained on the smooth substrate to the well-known dataset obtained by Ujereh et al. \[135\], as well as to classical model, including the one for nucleate boiling heat transfer by Rohsenow \[136\] and the one for critical heat flux by Zuber \[137\] (Figure 12).
Figure 12: Comparison between the boiling curve measured on silicon smooth surface in the present study and the one obtained by Ujereh et al. [135]. The solid line represents the heat flux predicted by Rohsenow model, and the dashed line represent the critical heat flux predicted by Zuber model [137].
3.3 Results and Discussion

3.3.1 Enhancement in Critical Heat Flux and Nucleate Boiling Limit.

We systematically varied the height $l$ of nanopillars fabricated on silicon substrates (Figure 11) and showed that increasing $l$ resulted in the enhancement of both the critical heat flux (CHF) and the upper limiting temperature of nucleating boiling. The nanopillars were fabricated by an inductively coupled plasma reactive ion etching (ICP-RIE) process that directly modified the surface. No coating layers were added which could induce additional thermal resistance to the substrate [138]. Typically, the quantity used for characterising the upper limiting temperature is either the CHF temperature $T_c$, or the Leidenfrost temperature $T_L$. The nanopillars were arranged in a hexagonal lattice with the lattice pitch $p \approx 800$ nm, the base diameter of nanopillars $d_b \approx 440$ nm, and $l$ being varied from 260 nm to 1390 nm. The differences in boiling behavior and performance between these substrates therefore are attributed to variation in $l$, or alternatively the surface roughness $r = A_t/A_p$. Here $A_t$ denotes the total surface area due to the presence of the nanopillars, and $A_p$ is the projected boiling area. In our experiment, $r$ ranged from 1 for the smooth silicon substrate to 3.2 for the longest nanopillar substrate with $l = 1390$ nm. To qualitatively evaluate the effect of the nanopillars on boiling, we first compared the boiling behavior of the smooth substrate and the nanopillar substrate with $r = 3.2$ at several surface temperatures $T$ (Figure 13). Although the onset of boiling occurred at $T \approx 69 \degree C$ for both substrates, the size of bubbles generated on the smooth substrate varied much more broadly than that on the nanopillar substrate. The difference in bubble dynamics became even more contrasting at higher temperature. The bubbles on the smooth substrate tended to merge and create either large bubbles or vapor columns starting from the substrate. But those generated on the nanopillar substrate had much lesser tendency to merge and it seemed that they were more uniform in size. We note that it is unlikely for bubbles to coalesce after their detachment from the substrate due to liquid inertia and surface tension, thus the coalescence process mainly occurred between consecutive bubbles generated from the same nucleation site before detachment. This strongly suggests that resistance to coalescence, as well as the uniform size of bubbles
Figure 13: Representative snapshots showing boiling phenomenon on the smooth substrate (top panel) and the nanopillar substrate with $l = 1390$ nm (bottom panel) at several surface temperatures $T$. While the smooth surface produces vapor bubbles which have tendency to coalesce (e.g., at $T = 74^\circ C$) and form vapor columns (e.g., at $T = 78^\circ C$), the nanopillar substrate produce bubbles which have a narrow size distribution tend to evolve separately without merging. The vapor column and bubbles are highlighted by red dashed lines.
generated from the nanopillar substrate result from an effective rewetting process, which facilitates bubble detachment from the surface. We hypothesise that deviation in boiling behavior of nanopillar substrates from the smooth substrate, therefore, originates from the nanopillar-induced enhancement in the rewetting process.

We now quantify the effect of nanopillars on the boiling performance by measuring the heat flux $q$ for each substrate as a function of the superheat $\Delta T = T - T_b$, where $T_b = 56^\circ C$ is the boiling temperature of FC-72 at atmospheric pressure. The dependence of $q$ on $\Delta T$ for the smooth and all the nanopillar substrates is shown in Figure 14a. Starting from $\Delta T = 0$, $q$ first gradually increased due to natural convection until it reached the onset of nucleate boiling ($\Delta T \approx 30$ K for all tested substrates). In this natural convection regime, the presence of nanopillars had negligible effect on the heat flux, as the nanopillars were much smaller than the thermal boundary layer thickness. Here, the boundary layer thickness was roughly $57 \mu m$, estimated using the ratio between the natural convection heat transfer coefficient and the thermal conductivity of FC-72 [139].

As $\Delta T$ increased past the onset of nucleate boiling, the heat flux on nanopillar substrates, denoted as $q^n$, deviated substantially from that of the smooth substrate. In particular, $q^n$ after the system transitioned into the nucleate boiling regime was achieved at much lower superheat compared to that when system was still in the natural convection regime (inset of Figure 14a). For instance, for the substrate with $r = 2$, $q \approx 3.3 W.cm^2$ was achieved at $\Delta T \approx 16$ K when the system was in the nucleate boiling regime, whereas a slight increase in heat flux, $r = 2$, $q \approx 3.5 W.cm^2$, was achieved at much higher superheat $\Delta T \approx 33$ K in the natural convection regime. On the smooth substrate, however, the heat flux increased smoothly as the system transitioned into the nucleate boiling regime. The presence of nanopillars caused a substantial jump in heat flux as soon as the system transitioned to the nucleate boiling regime because the heat transfer mechanism was more efficient for the nanopillar substrates. The sudden discontinuity in the boiling curve was seen because of the homogeneous spread of nucleation sites, high generation frequency and narrow size distribution of bubbles on nanopillar substrates. With the superheat increasing beyond the onset of nucleate boiling, bubbles were generated with higher frequency and larger size, intensifying forced convection in the bulk liquid and subsequently enhancing the heat flux $q$. For each substrate, $q$ increased
to the CHF $q_c$ at the critical temperature $T_c$, beyond which it dropped sharply due to excessive vapor generation and lack of replenishing liquid to the substrate. The heat flux reached its minimum value at the so-called Leidenfrost temperature $T_L$, or the upper limit of nucleate boiling. The sudden drop in heat flux at $T_L$ often triggers drastic spike in surface temperature causing the notorious “burn-out” in boiling applications. Thus designing heat-dissipating substrates with high $T_L$ is as practically important as enhancing the critical heat flux.

We observed considerable enhancement in both $q_c$ and $T_L$ on nanopillar substrates. The dependences of $q_c$ and $T_L$ on the surface roughness $r$ is shown in Figure 14b. Both $q_c$ and $T_L$ increased monotonically with the increase of $r$ (or equivalently with pillar height $l$). Compared to the smooth substrate ($r = 1$), $q_c$ and $T_L$ on the nanopillar substrate with $r = 3.2$ increased $\approx 50\%$ and $\approx 25^\circ C$, respectively. The enhancement in both $q_c$ and $T_L$ is a remarkable feature of the nanopillar substrates as opposed to those fabricated with larger scale structures. It was observed that micro-structures only enhance the heat flux without increasing the Leidenfrost temperature; typically $T_L$ decreases with increasing height of microstructures [140]. Separate investigations on hierarchical substrates, i.e., microstructured surfaces covered with nanograss, reported enhancement in either the Leidenfrost temperature [141, 142, 143], or the heat flux [120, 142, 144, 145, 146, 147, 148, 149].

### 3.3.2 Mechanism of Heat Transfer Enhancement on Nanopillar Substrates.

To understand how the nanopillars enhanced $q_c$ and $T_L$, we investigated the heat transfer mechanism on nanopillar substrates. Based on the qualitative observations of the differences in bubble generation between the nanopillar substrates and the smooth one, we postulated that the major contributing factor leading to the observed change in $q_c$ and $T_L$ is the nanopillar-induced rewetting process. For hierarchical structured surfaces, i.e., microstructures covered by nano-grass, enhancement in $q_c$ was observed. However it was attributed to the wicking process. More liquid was brought to the surface due to the enhancement in
volume of liquid wicking through the microstructures, which resulted in an increase in heat flux by latent heat of evaporation. Because of the tremendous viscous stress induced in flows confined in such small length scales between pillars, [120] the wicking process is not possible for nanopillar substrates.

We focused on the advancing contact line of liquid to study the nanopillar-induced rewetting process and its effect on the enhancement of heat transfer. As shown in Figure 15, the rewetting process of vapor bubbles and the spreading process of liquid are similar. Taking advantage of this similarity, the dynamics of the advancing contact line can be studied separately in the case of spreading liquid on nanopillar substrates [122, 129]. The rewetting process has been studied extensively [120], which revealed contributing factors such as surface-induced capillary force [120], hydrostatic and hydrodynamic forces [129], reshaping effects [150], vaporisation [151]. For the nanopillar substrates, we investigated the spreading of liquid from a capillary tip onto heated substrates (Figure 15a) and determined the dominant effects responsible for the heat transfer. The surface temperature was varied. The temperature dependence of the apparent spreading velocity $v_s$ on each nanopillar substrate was determined by tracking the three-phase contact-line (TCL), when the liquid was spread-
Figure 15: (a) Schematics showing that the rewetting process in pool boiling (left panel) is similar to the spreading process (right panel), in particular in the motion of liquid at the three-phase contact line (middle panel). (b) Apparent spreading velocity $v_s$ of FC-72 on different substrates over a range of temperature from $20^\circ$C to $46^\circ$C.
ing. The surface temperature can be varied from room temperature $T_r = 20^\circ C$ up to $46^\circ C$ without causing the liquid to boil. Although the displacement of the TCL results from various coupled effects, we simplified the analysis by decomposing $v_s$ into several independent components (Figure 15b):

$$v_s = v_{ca} - v_n - v_h,$$

(3.3)

where the component $v_{ca}$ is caused by capillary force on the substrate and therefore is a function of the surface roughness $r$ only. The component $v_h$ represents the reduction in spreading velocity as liquid absorbs heat from the surface and evaporates. Thus at room temperature $v_h = 0$, as there is no heat transferred from the surface to the liquid. The velocity component $v_n$ represents the reduction in spreading velocity due to natural evaporation of liquid. In the case of boiling, it vanishes as bubbles generated during boiling of liquid are filled only with saturated vapor. Here, we neglected contributions to TCL displacement from hydrostatic pressure of the liquid column, and from capillary pressure at the upper liquid surface in the tube due to the small gap between the capillary tube and the substrate.

We postulate that nanopillar-induced enhancement in wetting increases the heat flux on nanopillar substrates. This is suggested from the linear correlation between the critical heat flux of different substrates and the spreading velocity $v_s$ measured on respective substrates at surface temperature $T = 20^\circ C$. In other words, the presence of nanopillars intensifies the rewetting process, leading to an added amount of liquid brought to and subsequently evaporated from the surface. Among the contributing components to the apparent spreading velocity, $v_{ca}$ inherits the effect of $r$ on capillary wetting, thus has a direct relation to the enhanced rewetting process. In addition, as the surface temperature for spreading liquid was set lower than the liquid’s boiling temperature, we assume that with constant surface temperature, $v_n$ remains fixed for all the substrates, i.e., $v_n^n = v_n^s$, where the superscripts $n$ and $s$ respectively indicate quantities of the nanopillar substrates and the smooth substrate. We recall that $v_{ca}$ is independent of $T$ and $v_h = 0$ at room temperature. As a result, at room temperature $T_r$, the spreading velocity difference $\delta v_s(T_r) = v_{ca}^n(T_r) - v_{ca}^s(T_r)$ between a nanopillar substrate and a smooth substrate only depends on the change in capillary velocity between the two substrates $\delta v_{ca} = v_{ca}^n - v_{ca}^s$. Thus, $\delta v_{ca}$ can be estimated as $\delta v_{ca} \approx \delta v_s(T_r)$. We measure the spreading velocity $v_s$ for all nanopillar substrates and the smooth substrate
The spreading velocity increase $\delta v_s(T_r)$ is calculated for each nanopillar substrate to obtain $\delta v_{ca}$. The spreading velocity increases with increasing nanowire height due to the increasing energetic favorability of wetted nanowire surfaces of increasing height. The energy of the different dry nanopillar substrates is approximately the same. However, the energy of different wetted nanopillar substrates decreases with increasing height due to the larger interface between the liquid and solid nanopillar array. This energy difference drives the spreading of the FC-72, and thus, the spreading velocity increases with increasing nanopillar height.

We note that the heat flux at CHF on smooth substrates depends on the surface temperature and can be predicted using the classical model for nucleate boiling by Zuber [137]. A comparative study between the model and our boiling data on the smooth substrate shows an excellent agreement (Figure 12). The results of the nanopillar substrates also suggest that the boiling crisis is mainly dictated by the intensity of the rewetting process, and the increase in critical heat flux is a direct consequence of the faster rewetting velocity using longer nanopillars.

### 3.4 Conclusion

The boiling behavior in the nucleate boiling regime is significantly affected by the presence of nanopillars fabricated on boiling substrates. Both the heat flux and surface temperature at CHF can be enhanced by increasing the height of nanopillars. We attribute such enhancement to the nanopillar-induced increase in rewetting velocity. Based on the observations that the rewetting velocity increases for substrates with longer nanopillars, as well as the assumption that the enhancement in heat flux dominantly takes place at the three-phase contact line, a mechanistic model was developed to explain the increase in both the CHF and the temperature at CHF of nanopillar substrates. This model takes into account the nanoscales of the pillars, and thus, excludes the wicking motion, or imbibition of
fluid, as plausible mechanisms for heat transfer enhancement. The enhanced capillary force
due to the presence of nanopillars is the major cause of the intensified rewetting process
and subsequent increases in heat flux and temperature at CHF. The enhancement in both
of these critical quantities in pool boiling is a remarkable feature of nanopillar substrates in
comparison with nano/micro-engineered substrates in which only either one can be increased
and these results provide new insights regarding the design of textured substrate for boiling
applications.
4.0 Stable Lotus Leaf-Inspired Hierarchical, Fluorinated Polypropylene Surfaces for Reduced Bacterial Adhesion

4.1 Introduction

Plastics are used in a wide range of medical components such as prosthetics, implants, catheters, and syringes, due to their chemical resistance, versatility in manufacturing, high specific strengths, and low cost [152]. However, contaminating bacteria can attach to plastic surfaces and grow and form biofilms that lead to healthcare associated infections [153]. The consequences on patients and their families are serious, as infections can extend hospital stays, create long-term disability, increase healthcare costs, and even result in unnecessary deaths [154, 155]. In the United States alone, there are 90,000 deaths associated with healthcare-associated infections every year [156] These issues are even worse in developing countries where resources and accountability are poor [157]. Bacteria cause infections by attaching to a surface and forming organized and multicellular biofilms. Two strategies for creating antibacterial surfaces are (1) bactericidal surfaces that kill bacteria cells that come in proximity of or contact the surface and (2) anti-biofouling surfaces that make the bacterial attachment process difficult. In this study, we focus on modifying polypropylene (PP), which is a thermoplastic suitable for use in clinical environments due to its unique rigidness, chemical solvent resistance, and ability to withstand high temperatures compared to other polymers [158]. PP is commonly used for injectors, syringes, medical packaging and cases for contact lenses [159, 160, 161, 162, 163] and is expected to be the fastest growing plastic for medical packaging [164]. Many bactericidal PP surfaces have been studied by incorporating silver nanoparticles-zeolite plastics [165], copper nanoparticles [166, 167], and silver nanoparticles [168, 169]. However, nanoparticles are easily removed by abrasion [170, 171] and the metal ions eventually leach out of the surface completely, rendering the surface sterile against bacteria. Metal ions may also be toxic to aquatic organisms and the environment [172, 173]. Furthermore, bactericide agents must be used in high concentration because many bacteria can sustain growth in low concentrations [174]. Anti-biofouling
PP surface modifications have been investigated to combat these issues. PP membranes have been fabricated by the UV-induced grafting of zwitterionic anti-fouling polymers and demonstrated a 77% reduction in *Escherichia coli* (*E. coli*) adhesion [175]. Anti-biofouling PP surfaces have also been prepared by thermal annealing to create microscale patterns of rice that reduce the adhesion of *E. coli* by 53% compared to controls [176]. In this study, we examined how different reactive ion etching (RIE) processes affect the anti-biofouling properties of PP samples. Our reactive ion etching method provides a single step approach without the need for patterning or the incorporation of additional materials. We studied how different oxygen and fluorine reactive ion etching (RIE) treatments affect the surface chemistry, morphology, and wettability, and bacteria adhesion of PP. We found that a light power oxygen etching treatment creates a hydrophilic surface that reduces bacteria adhesion of *E. coli* by 68.7% compared to untreated PP. Etching a PP surface with high power oxygen creates a surface with about the same surface energy, but nanofibril structures with microscale roughness. These structures exhibit increased bacteria adhesion due to a combination of greater microscale roughness and air pockets that reduce the effectiveness of the liquid barrier. In contrast, we demonstrate substantially reduced bacteria adhesion through lotus-leaf-inspired low surface energy, hierarchical microstructure/nanofibrils in PP. These surfaces exhibit lotus-leaf-like wetting with high static water contact angle (155°) and low hysteresis (less than 10°). Water droplets easily roll off these surfaces as opposed to the other PP samples. Furthermore, these lotus-leaf-like surfaces reduce *E. coli* by 99.6% compared to untreated control samples. These surfaces demonstrate water contact angle stability over a week in contrast to hydrophilic samples, where the contact angle degrades after just one day.
4.2 Methods

4.2.1 Materials

PP sheets were purchased from an online vendor (Small Parts), which have a standard tolerance and meet ASTM D4101-PP0112 specifications [177]. The thickness of the PP sheet was 1.57 mm. Electronic grade acetone (99.5%), methanol (99.9%) and isopropyl alcohol (99.5%) were bought from VWR. Diiodomethane (99%) was bought from Sigma-Aldrich. Deionized water was obtained from a Millipore Academic A10 system with total organic carbon below 40 ppb.

4.2.2 Sample Preparation

Circular coupons with 12.7 mm diameter were made from the PP sheet using a custom-made hole punch. Afterwards, the samples were cleaned with acetone, methanol, and isopropyl alcohol and dried with nitrogen gas. All samples including the control were cleaned with a low power argon plasma (Diener Electronic GmbH) using diffusion process plasma cleaning. The plasma clean parameters for all samples were set to power = 20 Watts, pressure = 100 mTorr, flow rate = 30 sccm and duration = 70 sec. Then, experimental samples were treated by reactive ion etching (Trion III). Two types of samples were prepared by oxygen treatment. Both oxygen treatments were performed under pressure = 100 mTorr, O2 flow rate = 98 sccm, and duration = 120 sec. However, one treatment had high power (HP) of 200 Watts and the other had a low power (LP) of 25 Watts. The fluorinated samples were initially treated with oxygen for 70 seconds and then treated with CF4 and SF6 gasses in order to maximize fluorination at power = 200 Watts, pressure = 250 mTorr, CF4 flow rate = 86 sccm, SF6 flow rate = 52 sccm, and duration = 1800 sec (or 30 minutes).

4.2.3 Surface Characterization

Morphology Characterization The physical morphology of PP surfaces was characterized by scanning electron microscopy (SEM, Zeiss Sigma 500 VP) and atomic force
microscopy (AFM, Multimode SPM with a Digital Instruments Nanoscope III controller). For SEM imaging, the samples were sputter coated with 7 nm gold/palladium (80:20) using a sputter coater (Hummer), as the polymer samples were non-conductive. For AFM, the PP surfaces were imaged in tapping mode, using silicon nitride tips to assess surface topography and roughness in 20 µm by 20 µm areas. The AFM tip had a radius of 8 nm, and the total tip height was 12-18 µm. Data analysis was performed with Digital Instruments version v720 and Gwyddion software. Additionally, dimensional stability was tested with the ASTM D1204 standard (except with 3 inch by 3 inch samples) by comparing the dimensions of samples before and after RIE treatment [178]. Measurements of the sample width and length before and after plasma treatments were conducted using a digital vernier scale caliper.

**Contact Angle Measurements and Surface Energy Calculation** Static water contact angles (WCA) for all the surfaces were measured using a video contact angle goniometer (VCA 2000 Optima XE). This goniometer utilizes a precision camera and advanced PC technology to capture static or dynamic images of the droplet and determine tangent lines for the basis of contact angle measurement. Contact angle measurements were taken in ambient air at 2225 °C and 2030% relative humidity. Contact angle measurements were taken from 5 µl droplets of deionized water. Similarly, the hysteresis was tabulated for each treatment by measuring the advancing and receding contact angles during syringe controlled water dispersion and withdrawal, respectively. Hysteresis is defined as the difference between the advancing and receding contact angle. The fractional surface areas in analyzing different wetting states were calculated using MATLAB Image Processing Toolbox.

**X-ray Photoelectron Spectroscopy** All samples were analyzed by x-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250 Xi multichannel) with monochromatic Al K radiation. XPS was performed at an acceleration voltage of 15 kV with an emission current of 15 mA, in a residual vacuum of approximately 1 × 10⁹ Torr. The analyzer was used in fixed analyzer transmission (FAT) mode. The spectra were taken from two areas on each sample, and a minimum of two replicate samples were analyzed for each recipe. Sample surface compositions were determined from the average of these measurements.
4.2.4 Bacterial Adhesion Experiments

Adhesion to surfaces was tested using a fluorescent bacterial strain. To generate a fluorescent bacteria, *E. coli* K-12 strain W3110 was transformed by electroporation with GFP expressing plasmid pGFPmut2 [179, 180]. Cultures of the fluorescent *E. coli* were grown in 5 ml of LB broth at 30°C for 18-20 hours with aeration and normalized to OD$_{600}$ = 0.1 using saline (NaCl 0.9 %) in a spectrophotometer (SpectraMax M3) [181]. Coupons were glued to the bottoms of the wells of 12 wells plates as previously described and the silicon sealant was allowed to dry for 30 minutes [182]. The wells were then filled with 2.5 ml of the fluorescent bacteria in saline. After 30 minutes at 37°C, the saline was removed, and the coupons were rinsed three times with 2.5 ml of saline to remove non-adhered bacteria. The exposed coupon surface was then placed under a coverslip and observed by fluorescent microscopy (Nikon TE2000-E microscope with a Photometrics CoolSNAP HQ-camera and a 20X objective). NIS-Elements 3.2 software was used to obtain digital images that were then analyzed for the number of attached bacteria using ImageJ software (NIH). In some cases a few loosely attached bacteria cells were observed, which were moving on the surface. Those were manually calculated and subtracted from the counts obtained from ImageJ counts, and these bacteria represented less than 10% of the total bacteria in all cases. The field of view for each picture was 350 μm by 265 μm. Approximately 10 images were taken across the mid-point of each coupon from side to side to gain representative data and eight separate coupons of each type were read for each experiment.

4.3 Results and Discussion

4.3.1 Fabrication

In this study, both oxygen plasma treated hydrophilic and fluorine treated hydrophobic PP samples were investigated. Oxygen plasma tends to render the surfaces hydrophilic, while fluorine tends to make the surface hydrophobic. Both types of RIE treatments were studied as surface wetting properties have been observed to have a significant impact on
bacterial adhesion [183] and both hydrophilic [184] and hydrophobic [185] surface functionalization have been utilized previously to reduce bacterial adhesion. RIE recipes of different samples were tuned for a range of observable wetting results from plasma modified PP. The RIE process modifies the surface morphology from a combination of physical and chemical reactions with the substrate due to the prolonged surface bombardment of activated ions in a controlled environment. We varied the power to prepare two types of oxygen treated samples having similar hydrophilicity, but different surface morphology. Initially, three types of fluorination recipes were evaluated, using only CF4, only SF6 and a combination of both gases, to prepare the hydrophobic samples. Different durations of 10, 30, and 60 minutes were also tested. An optimized recipe for obtaining superhydrophobic samples (in terms of highest contact angle) were obtained while CF4 and SF6 were set at 86 and 52 sccm, respectively for a 30 minute duration.

4.3.2 Surface Characterization

The surface topography and surface chemistry was altered by plasma ion bombardment during the RIE process. The physical morphology of PP surfaces was characterized by SEM. Figure 16 shows the top view and Figure 17 shows the 75° tilted view of SEM images of each types of samples. These images demonstrate the difference in surface morphology of the control (Figure 17a), LP oxygen sample (Figure 17b), HP oxygen sample (Figure 17c), and fluorinated sample (Figure 17d). The surface of the untreated control samples and the LP oxygen treated samples look similar and are both relatively smooth. On the other hand, the surface of HP oxygen treated samples show nanofibril structures. The HP oxygen PP surface morphology consists of dense forests of nanofibrils about 40 nm diameter and 1 μm height. The fluorinated samples have hierarchical features, with microstructures of about 1 μm in height and nanofibrils of about 30 nm diameter of about 0.5 μm height. These nanofibrils are not as dense as the HP oxygen treated samples.

The surface morphologies of the four types of samples were further characterized by AFM (Figure 18a). The surface morphology was characterized by the root mean square (RMS) roughness and the power spectral density function. The RMS value of the surface
Figure 16: Top view SEM images of different samples: (a) Control, (b) LP oxygen, (c) HP oxygen, and (d) fluorinated samples. All images were taken at same magnification level.
Figure 17: 75° tilted view SEM images of different samples: (a) Control, (b) LP oxygen, (c) HP oxygen, and (d) fluorinated samples. All images were taken at same magnification level.
roughness of the control, LP oxygen treated, HP oxygen treated, and fluorinated samples were 20, 37, 230, and 154 nm respectively. While the untreated and LP oxygen treated samples are relatively flat, the HP oxygen treated samples and the fluorinated samples have much more roughness. Figure 18b plots the roughness power spectral density as function of the roughness wavelength. The HP oxygen sample has more roughness across all length scales compared to the LP oxygen sample. For length scales below $1 \mu m$, the surface is self-affine or fractal [186] as the power spectral density has a power-law dependence on the spatial frequency of roughness. For roughness wavelengths above $1 \mu m$, the power spectral density is fairly flat. In contrast, the fluorinated PP samples are self-affine across almost the entire roughness wavelengths shown, ranging from $20 \mu m$ down to 100 nm. This self-affinity across multiple length scales is also present in lotus leaves [187] and why we describe these surfaces as hierarchical.

The dimensional stability of the PP was also evaluated after RIE. Morphological changes may occur in thermoplastics from high temperature treatments due to the mismatch between the thermo-elastic properties of the polymer matrix and fibril structures [188]. The mean dimensional changes of LP oxygen treated, HP oxygen treated, and fluorinated samples were $0.03\% \pm 0.05\%$, $-0.42\% \pm 0.23\%$, and $0.13\% \pm 0.10\%$, respectively. All types of samples were dimensionally stable with negligible changes in length and width after the corresponding reactive ion etching treatments.

Figure 19 shows static water contact angle (WCA) results on the four different types of samples during WCA. The static WCA was measured for 3 samples of each type at 3 random spots per sample. The numbers in the figure denote the mean and standard error among treatments. The WCA was $98 \pm 0.9^\circ$ for the control samples where the $\pm 0.9^\circ$ refers to the standard error of the 9 measurements. Both types of samples prepared by oxygen treatment were hydrophilic. The LP oxygen treated samples had WCA of $51 \pm 1.3^\circ$ and HP oxygen treated samples had WCA of $72 \pm 1.5^\circ$. On the other hand, the fluorinated samples are superhydrophobic with a WCA of $156 \pm 0.6^\circ$.

The advancing, and receding contact angle of the four samples were further characterized. Figure 20 shows the results of this characterization where 3 samples were again measured 3 times each. The hysteresis is the difference between the advancing and receding contact
Figure 18: (a) 3-D plots by AFM show physical surface at microscale of different samples (i) Control, (ii) LP oxygen, (iii) HP oxygen, and (iv) fluorinated, (b) Power spectral density of four samples as a function of roughness wavelength.
The hysteresis was fairly high for the control sample and the oxygen treated samples, which are indicative of strong adhesion between the water and PP. These three samples may all be turned upside down with the water droplet still adhering to the substrate (Figure 20 images). On the other hand, the contact angle hysteresis for the superhydrophobic samples was approximately less than 10°, suggesting that the adhesion force between the liquid and surface is weak [189]. The water droplets easily roll off these surfaces with the slightest tilt. This combination of high WCA and low hysteresis is referred to as the lotus leaf wetting state and an indicator of self-cleaning ability [189].

The total surface energy of different samples was calculated from Fowkes method experiments, where the contact angle of diiodomethane, $\Theta_{DIM}$, and water $\Theta_{H2O}$ were used to calculate the total surface energy values (Table 5). Static contact angles of diiodomethane (DIM), a purely dispersive liquid, were measured together with those of water, a highly polar liquid [190]. The independent dispersion and polar surface energy components for each sample type are calculated using Youngs and Dupres definition of adhesion equations. These quantities are summed for the overall surface free energy [191, 192]. Youngs contact angles were obtained from the observed contact angle values and corresponding wetting state equations. For the Wenzel wetting state,

$$cos(\theta_W) = rcos(\theta_Y)$$

\[4.1\]
Figure 20: Contact angle hysteresis of different samples and images of 180° tilted samples. No image is obtained for the Fluorinated sample as water droplets easily roll off these surfaces with the slightest tilt.

where $\theta_W$ is the observed contact angle in the Wenzel wetting state and $\theta_Y$ is the Young’s contact angle. In the Cassie-Baxter wetting state,

$$\cos(\theta_{CB}) = rf\cos(\theta_Y) - (1 - f) \quad (4.2)$$

where $\theta_{CB}$ is the observed contact angle in the Cassie-Baxter wetting state. $r$ is the roughness ratio factor and $f$ is the solid-liquid fractional surface area where $1 - f$ is the solid-air fractional surface area. The flat control and LP oxygen samples are in the Wenzel wetting state due to the relatively flat surfaces. In the Wenzel wetting state, the roughness parameter enhances the intrinsic wetting property of a surface, while in the Cassie-Baxter wetting state the roughness always make the surface more hydrophobic. The observed wetting behavior of the HP oxygen samples suggests that they are in the Cassie-Baxter wetting state. In addition, the fluorinated samples must be in the Cassie-Baxter wetting state due to the superhydrophobic behavior of the surface. The mean and standard error of these values are shown in the table. The surface energy, $\gamma$ is the sum of the dispersive and polar component of surface energy. The fluorinated samples are superhydrophobic due to a combination of low surface energy and hierarchical surface structures. In contrast, the oxygen treated samples have high surface energy, explaining the lower static contact angles and higher hysteresis.
Table 5: Roughness ratio factor ($r$), solid-liquid fractional surface area ($f$), and Youngs contact angle ($\Theta_Y$), Diiodomethane (DIM) contact angle ($\Theta_{DIM}$), water contact angle ($\Theta_{H_2O}$), surface energy of different samples ($\Omega_S$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$r$</th>
<th>$f$</th>
<th>$\Theta_Y$ (Degree)</th>
<th>$\Theta_{DIM}$ (Degree)</th>
<th>$\Theta_{H_2O}$ (Degree)</th>
<th>$\Omega_S$ (mNm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>1.03</td>
<td>1</td>
<td>98.2</td>
<td>60 $\pm$ 2.2</td>
<td>98 $\pm$ 0.9</td>
<td>28.4 $\pm$ 2</td>
</tr>
<tr>
<td>LP Oxygen</td>
<td>1.11</td>
<td>1</td>
<td>55.3</td>
<td>62 $\pm$ 2</td>
<td>51 $\pm$ 1.3</td>
<td>46.7 $\pm$ 2.3</td>
</tr>
<tr>
<td>HP Oxygen</td>
<td>3.02</td>
<td>0.38</td>
<td>36</td>
<td>13.5 $\pm$ 3.0</td>
<td>72 $\pm$ 1.5</td>
<td>59.6 $\pm$ 2.2</td>
</tr>
<tr>
<td>Fluorinated</td>
<td>2.63</td>
<td>0.21</td>
<td>103.2</td>
<td>110 $\pm$ 4.4</td>
<td>156 $\pm$ 0.6</td>
<td>12.9 $\pm$ 2.2</td>
</tr>
</tbody>
</table>

Table 6 summarizes our XPS results. It was observed the fluorinated samples had 55% fluorine on the surface. The untreated samples did not have any fluorine, while the LP oxygen treated samples had very small amount fluorine (0.85%). However, the HP oxygen treated samples had higher amount of fluorine (5%) compared to the control and LP oxygen treated samples. The presence of fluorine in our HP and LP oxygenated samples are possibly due to the presence of fluorine in the chuck and backstreaming of oil during the RIE process. XPS survey scan of different samples are shown in Figure 22-25.

Contact angles were measured over a week of time for all samples to check the stability (Figure 21). The standard error was always within 2$^\circ$ for control, LP oxygen treated and fluorinated samples, while it was a little higher (4$^\circ$) for HP oxygen treated samples. The LP and HP oxygen treated samples were observed to have decreasing hydrophilicity in ambient conditions after just one day. This is likely due to particulates landing on the high energy surface. However, the fluorinated samples demonstrated stable superhydrophobicity over a week as the mean contact angle was always higher than 146$^\circ$. The fluorinated samples were also observed to be chemically stable in ambient conditions for over a week. XPS analysis was conducted after one week of sample preparation and showed negligible change in atomic percentage of fluorine, demonstrating that the fluorine ions on the surface are stably bounded from polar covalent carbon-fluorine bonds formed after treatment (Figure 26).
Table 6: XPS surface chemical analysis of the various surfaces

<table>
<thead>
<tr>
<th>Name</th>
<th>C 1s</th>
<th>O 1s</th>
<th>N 1s</th>
<th>F 1s</th>
<th>Si 2s</th>
<th>Al 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>88.35</td>
<td>9.55</td>
<td>0.73</td>
<td>0</td>
<td>1.37</td>
<td>0</td>
</tr>
<tr>
<td>LP Oxygen</td>
<td>82.16</td>
<td>13.89</td>
<td>0.75</td>
<td>0.85</td>
<td>0.97</td>
<td>1.38</td>
</tr>
<tr>
<td>HP Oxygen</td>
<td>66.39</td>
<td>21.09</td>
<td>1.38</td>
<td>5.51</td>
<td>1</td>
<td>4.63</td>
</tr>
<tr>
<td>Fluorinated</td>
<td>43.19</td>
<td>0.86</td>
<td>0.68</td>
<td>55.27</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 21: Water contact angle of different samples over time.
Figure 22: XPS survey scan of control sample.

Figure 23: XPS survey scan of LP Oxygen treated sample.
Figure 24: XPS survey scan of HP Oxygen treated sample.

Figure 25: XPS survey scan of Fluorinated sample.
Figure 26: Comparison of XPS survey scan of fresh fluorinated samples (top) and 1-week old fluorinated samples (bottom).
4.3.3 Results of Bacterial Adhesion Tests

Figure 27 shows the results of the bacterial adhesion experiments and fluorescent representative images of different treated samples with bacteria. Bacterial adhesion was evaluated by fluorescent optical microscopy. Afterwards, ImageJ software was used to count the number of bacteria cells that adhered to the surface. The number of bacteria cells per millimeter squared is plotted for each sample type. Eight coupons were characterized for each RIE treatment. The red solid line represents the mean count, the pink region represents the standard error around the mean, and the black circles represent individual data points. Results show the difference between the LP oxygen treated samples ($1209 \pm 120 \text{ cells/mm}^2$) and the HP oxygen treated samples ($5176 \pm 835 \text{ cells/mm}^2$). The LP oxygen treated samples exhibit a decrease in adhered bacteria compared with the control. The decreased bacteria adhesion in these samples is because the hydrophilic surface energetically maintains a liquid barrier between the surface and the bacteria cells, hindering cell-to-surface contact [193, 194]. On the other hand, the adhesion of *E. coli* to the HP oxygen treated samples was much more than the control samples. While the surface energies of both types of samples are similar (Table 5), the surfaces of HP oxygen treated samples consist of dense nanofibrils in contrast to the relatively flat LP oxygen treated samples. The power spectral density of HP oxygen treated samples show a significantly higher frequency of roughness across all roughness wavelengths compared to the relatively flat LP oxygen sample. The increase in bacterial adhesion to the HP oxygen samples might be attributed to the increased wavelength roughness that is equivalent or larger than *E. coli* cells (rod-shaped about $2 \mu m$ long and diameter .25 to 1 $\mu m$). This roughness increases surface to cell binding sites. Furthermore, the HP oxygen samples contain air pockets that may decrease the effectiveness of the liquid barrier between the bacteria cells and surface. Indeed, these air pockets are why the water contact angle of the HP oxygen surfaces increase over that of LP oxygen surfaces. The effect of surface roughness on bacterial adhesion was studied previously. Harris *et al.* mentioned the effect of surface morphology on the adhesion of *Staphylococcus aureus* on the micro-rough and electropolished titanium surfaces [195]. Irregularities of polymeric surfaces promotes bacterial adhesion whereas ultra-smooth surfaces do not [196]. The size of roughness irregularities in
Figure 27: Bacterial counts per mm$^2$ for differently treated samples and fluorescent images of PP samples with adhered bacteria. The red solid line represents the mean count, error bars indicate standard error (n=8). a) Control, b) LP Oxygen, C) HP Oxygen, d) Fluorinated.
comparison to the size of the bacteria seems an important parameter. Previous study on bacterial adhesion reported that bacteria adhere more to irregularities that conform to the size of the bacteria, as this maximizes the surface area in contact with the cell [197]. Our HP oxygen samples had increased wavelength roughness that is equivalent or larger than *E. coli* cells and an increase in adhesion was observed for these samples. On the other hand, depressions or grooves too small for bacterium to fit into reduce the contact area of the bacterium, and hence adhesion [197].

The best results were obtained with fluorine plasma treated samples, which are lotus leaf-like. Lotus leaf surfaces are superhydrophobic due to their micron-sized papillae with nanometer-size protrusions and low surface-energy layer of epicuticular wax [198]. These structures are known to resist fouling from soil or dust [199, 200, 201]. Likewise, our treatment creates hierarchical microstructure/nanofibrils from a fluorine plasma etch process and the fluorination provides low surface energy. These PP surfaces exhibit lotus-leaf wetting due to a combination of high water static contact angle and low hysteresis. The number of bacteria cells adhered to the fluorinated samples (15 ± 10 cells/mm²) was extremely low, 99.6% less than the control samples (3860 ± 673 cells/mm²). Under the fluorescent microscope, barely any bacteria cells could be seen on these samples. The nanofibrils are smaller in size than bacteria and together with low surface energy significantly reduce the number of adhesion sites for *E. coli* cells. These fluorinated PP samples emulate the lotus leafs self-cleaning ability. Statistical analysis (Two-Sample t-Test) was done to evaluate the significance of the anti-biofouling performance of the various samples. The p values were 0.006, 0.242, and 0.001 when the control was compared to the LP oxygen treated samples, HP oxygen treated samples, and the superhydrophobic, lotus-leaf like fluorine treated samples, respectively.

### 4.4 Conclusion

We studied how reactive ion etching modifies the surface of PP samples and affects bacterial adhesion. The effect of different reactive ion etching recipes on morphology, surface energy, and wettability was also investigated. The bacteria adhesion on the LP oxygen
treated samples was significantly lower compared to the HP oxygen treated samples. The best anti-biofouling results were obtained from fluorine reactive ion etched samples that created lotus leaf-like hierarchical structures consisting of microstructures and nanofibrils. These PP surfaces exhibit super hydrophobicity, low hysteresis, and 99.6% less adhesion of *E. coli* than control samples. The combination of low surface energy and hierarchical morphology reduces the number of active sites for *E. coli* to adhere to the treated PP, emulating the lotus leaf self-cleaning effect.
5.0 Bactericidal Effect of Silicon Nanostructured Surfaces

5.1 Introduction

There is a great need for antibacterial surfaces that may reduce infections and illness in healthcare applications such as medical devices, sutures, contact lens cases, dental implants and catheters [202, 203, 204, 205, 206, 207, 208] as well as everyday household items such as kitchen and bathroom surfaces, appliances [209, 210], consumer hygiene products, health club equipment, and food packaging. The most widely used strategy has been the use of some sort of antimicrobials such as organic compounds like triclosan and zinc pyrithione [211, 212] or metallic ions such as Ag\(^+\) [213]. However, this approach suffers from drawbacks such as high-cost, short-term efficacy, and biological and/or environmental toxicity [214, 215, 216]. Bacteria have also evolved resistance and can sustain growth in the presence of low concentrations of antibiotics [217].

Recent nanofabrication approaches have been able to demonstrate bio-inspired antibacterial surfaces that either reduce bacteria adhesion or mechanically kill bacteria cells. The first approach uses a combination of surface nanotopography and surface functionalization to reduce bacteria adhesion [75, 218]. The second approach was inspired by the wings of insects (Psaltoda claripennis) wing surfaces are bactericidal to Pseudomonas aeruginosa cells [219]. However, cicada wing structures have demonstrated limited effect on rigid bacteria cells such as Gram-positive bacteria [220], which have a peptidoglycan cell wall about 4 to 5 times thicker than those of Gram-negative bacteria [221]. Ivanova et al. compared the bactericidal activity of black silicon to that of the wings of the dragonfly Diplacodes bipunctata [222]. Both the needle like structures on the surface of black silicon and the nanoprotrusions on the dragonfly wings form hierarchical structures and a mechanical bactericidal effect is observed. Hazell et al. used black silicon and diamond coated black silicon substrates with various surface morphologies and tested those surfaces against both Gram-positive and Gram-negative cells [223]. However, killing was only observed for Gram-negative cells. It is attributed to the difference in the thickness of the cell wall of Gram-positive bacteria.
compared to Gram-negative bacteria. The thickness of the cell wall of Gram-positive bacteria is around 20-80 nm, which consists of several layers of peptidoglycan. On the other hand, the cell wall of most Gram-negative bacteria is 5-10 nm thick, consisting of a single peptidoglycan layer [224]. This same phenomenon has been observed in other studies also, where the bactericidal effect against Gram-positive bacteria was negligible compared to that of Gram-negative bacteria [223, 225]. As previous studies found the gram positive bacteria difficult to kill, we concentrate on the killing of Gram-positive bacteria cells in the present study.

Infections due to bacterial adhesion is very common for implanted medical devices and extensive research is being done to address this issue. We focus on *Staphylococcus epidermidis* (*S. epidermidis*), a Gram-positive bacteria, which is a common source of infections on indwelling medical devices such as catheter. To evaluate the mechanical bactericidal effect on this bacteria, we prepared uniform and regular SiNC arrays. The morphology of these structures were varied and optimized. As mentioned earlier, the bactericidal nature of the nanostructures on cicada wings and black silicon, was demonstrated in recent research. But these random structures lack uniformity, both in terms of distribution of the structures and their shape. We have been able to fabricate uniform and regular nanostructured arrays with control over pitch, diameter, taper, and height. Nanosphere lithography (NSL) and combination of reactive ion etching (RIE) and deep reactive ion etching (DRIE) were utilized to prepare uniform silicon nanostructure arrays of different morphology. The objective of this current study is to investigate the impact of these parameters on the bactericidal performance of SinC arrays, while they are varied systematically. Our results demonstrate that these structures have a mechanical bactericidal effect on *S. epidermidis* and we present results on how morphology affects this killing rate.
5.2 Experimental Procedure

5.2.1 Fabrication of SiNC Substrates

P-type boron-doped (100) silicon wafer was used as substrate. The substrate was cleaned with acetone, methanol and isopropanol and then dried with nitrogen gas. Then polystyrene (PS) nanospheres were patterned on the substrate by the self-assembly method [226, 227, 228]. PS nanospheres were self-assembled in the air-water interface and then the monolayer was transferred to the substrate. After that the substrate was dried in air at room temperature. Then, reactive ion etching (RIE) with oxygen was used to reduce the diameter of the PS nanospheres. The pressure was set at 25 mTorr and the RF power was set at 25 W. The flow rate of oxygen was 25 sccm, which yielded an etch rate of 80 nm per minute. By varying the etch duration, it is possible to vary the diameters of the mask and hence that of the nanowires. After that we used the Inductively coupled plasma reactive ion etching (ICPRIE) to etch the silicon, while the PS nanospheres served as the mask for silicon. SF$_6$ was used as the etch gas and C$_4$F$_8$ was used as the passivation gas. After varying the ratio of the gases and observing the structure of the nanowires, the optimal ratio of the etch gas and passivation gas was determined to be 33 sccm : 82 sccm. The etch duration was varied to obtain nanowires of different height. Typically the height of the nanowires increased with an increase of etch duration. We observed tapering effects on the nanowires and all structures had different top and bottom diameters. Finally, we removed the PS nanospheres by ultrasonication in acetone for 5 minutes.

5.2.2 Bacterial Culture Preparation

A 5mL overnight culture was inoculated with a single colony from a streak plate and was incubated at 37°C for approximately 8 hours. A 50mL culture was then inoculated from the overnight culture in mid-exponential phase by combining 2mL of the culture and 48mL of peptone yeast-extract dextrose (PYD) in a 250mL baffled flask. The culture was incubated for 18 hours overnight at 37°C. The following day, the OD$_{600}$ was taken and proved to be 1.49 abs. The 50mL culture was transferred to a 50mL conical tube and was centrifuged at
5000g by repeated inversion. The bacterial culture was then diluted 1:10 in 0.01M PBS by combining 5 mL of the culture with 45 mL of 0.01M PBS in a new 250 mL flask. This new culture yielded an OD$_{600}$ of 0.1 abs.

### 5.2.3 Bacterial Experiment

For all samples, 10 $\mu$L of the 1:10 *S. epidermidis* PBS culture was aliquoted onto each substrate of 1.5 cm by 1.5 cm size. Separate samples were used for different time points. For the zero hour time point the culture was dropped and then withdrawn immediately from the substrates. For the one hour and three hour time points, the substrates were kept inside a humidity controlled environment after the culture was aliquoted for the specified amount of time. The relative humidity was maintained at nearly 100% to avoid evaporation. As complete recovery of the 10$\mu$L culture is difficult 90$\mu$L PBS was added and mixed well by pipetting before the 100$\mu$L was withdrawn. Then the bacterial culture was serially diluted 10-fold in 270$\mu$L of 1x PBS. Then 100ul was plated on PYD agar and spread with sterile glass beads. The bactericidal effect was evaluated in triplicate for both the bare silicon control and SiNC arrays. The plates were incubated at 37°C for 24 hours. Afterwards the plates were counted and CFU/mL counts were obtained. SEM was used to evaluate the surface of the used SiNC samples after the experiment.

### 5.3 Characterization of Fabricated Substrates

The physical morphology of the SiNC surfaces was characterized by scanning electron microscopy (SEM, Zeiss Sigma 500 VP). Top view, cross sectionl, and tilted view SEM images (Figure 28) were taken. The height, pitch and Tip diameter of different samples were measured using the SEM. Static water contact angles (Figure 29) for all the surfaces were measured using a VCA 2000 Optima XE video contact angle goniometer. This goniometer utilizes a precision camera and advanced PC technology to capture static or dynamic images of the droplet and determine tangent lines for the basis of contact angle measurement.
Table 7: Topographical parameters of SiNC substrates, as measured by SEM

<table>
<thead>
<tr>
<th>Sl</th>
<th>DRIE Duration(min)</th>
<th>Pitch(nm)</th>
<th>Top diameter(nm)</th>
<th>Height(µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32</td>
<td>1400</td>
<td>460</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>17</td>
<td>800</td>
<td>110</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>500</td>
<td>80</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>300</td>
<td>80</td>
<td>1</td>
</tr>
</tbody>
</table>

Contact angle measurements were taken in ambient air at 22-25 °C and 20-30 % relative humidity. Contact angle measurements were taken from 5 µl droplets of deionized water.

5.4 Results and Discussion

In order to study the pitch dependence of the SiNC substrates we fabricated samples of different pitch. The pitch of 4 types of samples were 300, 500, 800, and 1400 nm. The diameter of S. epidermidis, the bacteria used for the experiments, is 0.7-1 µm. Hence, the pitch of two types of samples were smaller than the diameter of the bacteria. The other two samples had pitch larger than or in the same level of magnitude compared to the bacteria. The height of the samples also varied due to the nature of the deep reactive ion etching process. From cross-section SEM images the height and top diameter of the structures were measured. The measurements have been tabulated in table 7. The height of the structures varied between 1 µm, and 6 µm, while the tip diameter varied between 80 nm, and 460 nm.

No difference in the CFU/mL counts was observed at the zero hour time point for any types of samples. As mentioned earlier the 10 µL bacterial culture was aliquoted and retrieved immediately to get the data for zero hour time point (Figure 30). It was done to ensure that no difference in the counts were observed because of the presence of the nanos-
structures only, when there was not sufficient time of interaction. The bactericidal effect for a particular type of sample was quantified by subtracting the number of surviving cells on the
substrate from the number of cells remaining in the bare silicon sample at the corresponding
time point. At the one hour time point bactericidal effect was observed only for the 300 nm
pitch samples. 20% killing was observed for these samples. For the other types of samples,
there was some natural variation. But the killing was not evident at the one hour time point.
At the three hour time point, some mild killing was observed for 800 nm and 1400 nm pitch
samples. Both of these samples exhibited around 10% killing of *S. epidermidis*. 500 nm
pitch samples had around 30% killed. While the best performance was observed for the 300
nm pitch samples. These samples had significantly reduced the number of viable cells and
the killing was measured to be around 82%.

The difference in the number of cells for different samples can be seen in Figure 31.
Among different reports regarding the bactericidal effects of nanostructured surfaces, some
reports suggested that the pitch of the nanostructures plays an important role in the bactericidal performance and an increase in bactericidal performance is observed associated with the variation of pitch. It has also been reported that there exists some optimal pitch, for which the best bactericidal performance is obtained [223]. Wu et al. studied the antibacterial properties of gold nanostructured surfaces and varied the height of these nanostructures [229]. They reported that structures with smaller height (50 nm) did not allow sufficient stretching/deformation of the cell membrane and most of the bacteria cells appeared alive. However, the minimum height of our structures was 1 µm, 20 times larger than this reported lower limit.

We observed the maximum death on the 300 nm pitch samples, which had the nanostructures with minimum height and maximum density. Figure 32 summarizes the results of our experiments at the 3 hour time point. The mechanism behind the bactericidal effects of nanostructured surfaces have been studied and different theories have been provided. We suggest that the stretching of the cell membrane is insufficient for cell rupture, when the pitch is larger than/comparable to the diameter of the *S. epidermidis* cells. The bacteria cells can settle down at the vacant large spacing among the nanostructures. This is verified by the SEM images (Figure 34), obtained after the experiment for the 800 nm and 1400 nm pitch.
Figure 31: Representative optical images of plates of the 3 hour time point after the 24 hour incubation period. (a) bare silicon, (b) 1400 nm, (c) 800 nm, (d) 500 nm, (e) 300 nm pitch samples.

samples. The small percentage of observed killing might be due to the direct penetration of the membrane by the nanostructures.

On the other hand, when the pitch is smaller than the diameter of the bacteria cell, there is not sufficient spacing among the nanostructures for the bacteria cells to settle down. The bacteria cells sit on top the nanostructures. Multiple nanostructures, present underneath individual cells for both 300 nm and 500 nm pitch samples, causes stretching of the bacterial cell membrane. Based on the number of nanostructures underneath the cells the stretching impact varies. The 300 nm pitch samples having a density of 2.8 times compared to the 500 nm substrates have a significantly higher impact in this regard. The cell death mechanism can be explained in the following manner. Because of the significant stretching impact on the
cell by the nanostructures of 300 nm pitch samples, the membrane is teared. The top surface of the spherical cell is flattened and lysis is observed. As a result of that significant killing is observed for the 300 nm pitch samples at the 3 hour time point, compared to that of the 500 nm pitch sample. SEM images in Figure 33 shows severely deformed lysed S. epidermidis cells observed on the 300 nm sample. These SEM images suggest the cytoplasmic materials inside the bacterial cell comes out after interaction with the nanostuctures, as the bacteria cells look completely flattened compared to their original spherical shape. The deformation and death of cells is evident from these images, as the flattened cells looks very much different compared to viable spherical S. epidermidis. 500 nm pitch samples, for which lesser amount of bactericidal performance was observed, can be seen in Figure 34a, and 34b. While many

Figure 32: Percentage of dead cells after 3 hour incubation of S. epidermidis on fabricated bacteridial samples. Error bars indicate standard error.
cells appeared viable and spherical, pore formation was observed for some bacteria cells. The similar effect was observed when bacteria cells were treated by ultrasound by Li et al. [230]. The SEM images of the 500 nm pitch samples with bacteria after pore formation in our study resembles their findings. The difference between the 300 nm and 500 nm pitch samples is that flattening of cell is not observed for the 500 nm pitch samples. That might be attributed to the difference in density of the nanostructures in these substrates.

5.5 Conclusion

SiNC substrates were fabricated by deep reactive ion etching. The height, pitch, top diameter of these structures were controlled. The bactericidal effect of these structures were
Figure 34: Tilted view SEM image of bacteria cell on different samples. 
(a,b) 500 nm, (c) 800 nm, (d) 1400 nm pitch samples.

tested against the Gram-positive bacteria, *S. epidermidis*. Gram-positive bacteria have a thicker cell wall compared to Gram-negative bacteria, and has been reported difficult to kill mechanically. SEM images revealed that the bacteria cells could sit in between the structures on samples with larger pitch, but not for the samples with smaller pitch. 300 nm pitch samples had the best results with bacterial killing of 82% at the three hour time point. As the bacteria cells develop resistance to drugs, these results provide insights towards an alternative approach to encounter this phenomenon.
6.0 Conclusions and prospects

Micro/nanostructured materials are quite useful due to their unique chemical, physical, and mechanical properties. In my work, I focused on simulation studies as well as the fabrication of micro/nanostructured materials to improve device performance. Our finite difference time domain simulation results showed that the absorption enhancement in vertical nanowire arrays over silicon thin films can be further improved through tilted nanowires. Tilted nanowire arrays exhibit improved absorption over the infrared, visible, and ultraviolet regime compared with vertical nanowires since the tilt removes symmetry requirements on the resonance modes in the nanowires. Incorporation of these structures could improve the efficiency of solar cells. We successfully fabricated wafer scale silicon nanopillar structures with different geometries. By using nanopillars with systematically varying heights on silicon substrates, we demonstrated scalable boiling enhancement with increasing height of nanopillars. Increasing the height of nanopillars effectively resulted in considerable enhancement of both heat flux and surface temperature at CHF. We attribute such enhancement to the nanopillar-induced increase in rewetting velocity.

We fabricated of micro/nanostructured materials with anti-biofouling and bactericidal properties. We reported on the micro-/nanostructuring and surface functionalization of PP substrates through various oxygen and fluorine reactive ion etching (RIE) treatments and their effects on wettability and bacteria adhesion. We found that oxygen treatment creates a hydrophilic surface that reduces bacteria adhesion compared to the control, but additional nanostructuring reduces the surface’s anti-biofouling properties due to increased microscale roughness and air pockets that reduce the effectiveness of the liquid barrier. Our best samples were prepared by a fluorine etch chemistry may be utilized to create lotus leaf-inspired, low surface energy, hierarchical micro-structure/nanofibrils in PP. Due to the low surface energy and hierarchical morphology, the surface exhibits lotus-leaf wetting (high contact angle and low contact angle hysteresis) where water droplets easily roll off the surface in contrast to other PP samples. The lotus leaf-inspired hierarchical, fluorinated surfaces exhibit a 99.6% reduction of \textit{E. coli} cell adhesion compared to untreated PP.
We then fabricated bactericidal surfaces consisting of uniform and regular nanostructured arrays. The pitch, diameter, taper, and height of the nanostructures are controlled. The bactericidal effect of these structures were investigated against Gram-positive bacteria (\textit{S. epidermidis}). Gram-positive bacteria have a thicker cell wall compared to Gram-negative bacteria, and has been reported difficult to kill mechanically. Our results shows that the center-to-center spacing among the pillars plays an important role in the bactericidal performance of the substrate. Significant enhancement in killing was observed for 1\,\mu m long, 300 nm pitch nanostructured surface with a tip diameter of 80 nm compared to the flat control substrates.

While our results are promising, there are still room for improvement. Increasing the height of nanopillars effectively resulted in considerable enhancement of both heat flux and surface temperature at CHF within the range of the heights we studied. However, there remains a question regarding the range of heights for which this effect would continue. As the spreading velocity might not increase indefinitely due to the competing effect of contact line friction with the increase of height of nanopillars. Similarly, the bactericidal results form our study can be used to fabricate improved nanostructured surfaces to exhibit complete killing of bacteria cells.
Appendix

A. Tilted Silicon Nanowire Array Simulation

We also studied the similar properties of the 500 nm long nanowires. The pitch $a$ was varied from 40 nm to 1000 nm and the diameter $d$ was also varied from 20 nm up to the pitch. The highest efficiency was obtained for 680 nm pitch and 640 nm diameter. The increase in efficiency for the 500 nm long nanowires was less than that of 1000 nm long nanowires. We also did the simulation study of the 500 nm long tilted nanowires. At 72.8° tilt angle the efficiency was maximum and the increase in efficiency was 6.47% compared to vertical ones.
Bibliography


