PHOTONICALLY ENHANCED AND CONTROLLED

POOL BOILING HEAT TRANSFER

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PHOTONICALLY ENHANCED AND CONTROLLED POOL
BOILING HEAT TRANSFER

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ABSTRACT

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The high cooling requirements from modern day electronic devices have given rise to a need for alternative heat dissipation methods. State of the art liquid to vapor phase change cooling schemes provide a cooling rate orders of magnitude higher than current single phase systems. Boiling studies have long been performed with the goal to enhance critical boiling parameters such as heat transfer coefficient (HTC) and critical heat flux (CHF) by altering surface morphology. More recently, the desire for active control of boiling processes has been realized due to transient and dynamic changes in system cooling requirements. A means of controlling the boiling process by manipulating surface energy through light excitation can provide the necessary adaptive heat transfer properties. In this study, photonically controlled pool boiling studies are conducted on copper, titanium dioxide, and carbon nanotube (CNT) samples. A significant variance in both HTC and CHF upon light excitation is observed in all samples, with different physical and chemical mechanisms for the change in surface
energy. Copper boiling samples were induced to a 35% decrease in CHF condition after several minutes using photonic energy via formation of hydrophobic nanoclusters of copper oxide. Photoactive titanium dioxide and CNT experiments showed a 16.8% decrease and 14.5% increase in HTC, respectively, upon light exposure. Small scale contact angle tests, scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS) on irradiated samples provide an insight into surface changes due to boiling and ultraviolet (UV) light exposure. In addition to photonically enhanced and controlled heat transfer experiments, a new technique for measuring liquid-solid contact during boiling using electrochemical impedance spectroscopy (EIS) is discussed.
I would like to dedicate this work to my mother and father, family, and friends, from which their consistent love and support this work would not have been possible.
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<th>Description</th>
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<tr>
<td>CHF</td>
<td>Critical Heat Flux</td>
</tr>
<tr>
<td>$h_{lv}$</td>
<td>Latent heat of vaporization</td>
</tr>
<tr>
<td>HTC</td>
<td>Heat Transfer Coefficient</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>MHF</td>
<td>Minimum Heat Flux</td>
</tr>
<tr>
<td>ONB</td>
<td>Onset of Nucleate Boiling Temperature</td>
</tr>
<tr>
<td>$q_H$</td>
<td>Heat flux at the heater dimensions</td>
</tr>
<tr>
<td>$q_S$</td>
<td>Heat flux at the surface dimensions</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>$T_{sur}$</td>
<td>Temperature at the boiling surface</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>$Z$</td>
<td>Impedance</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Receding contact angle in Kandlikar’s CHF Model</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Contact angle</td>
</tr>
<tr>
<td>$\theta_p$</td>
<td>Phase angle</td>
</tr>
<tr>
<td>$\lambda_T$</td>
<td>Taylor wavelength of instability</td>
</tr>
<tr>
<td>$\sigma_L$</td>
<td>Surface tension of the liquid</td>
</tr>
<tr>
<td>$\sigma_S$</td>
<td>Surface tension of the solid</td>
</tr>
<tr>
<td>$\sigma_{SL}$</td>
<td>Interfacial tension between solid and liquid</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Heater orientation</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION AND LITERATURE REVIEW

1.1. Thermal Management Motivation

Thermal management is limiting technological development in computing devices, military avionics systems, and other electronic applications. Thermal management schemes that have worked in the past involving single phase air or liquid cooling techniques are becoming inadequate with the increasing demand for higher cooling rates and much smaller electronic devices. As a result, thermal management schemes based on liquid to vapor phase change, which can dissipate much higher heat loads, are under consideration. The following sections describe the problem in more detail and explore technological solutions.

1.1.1. Thermal Management Issues with Computing Devices and Processors

The computer manufacturing industry has long been concerned with thermal management of processors in laptops, desktop computers, and other computing devices. Gordon Moore, co-founder of Intel and pioneer in the semiconductor industry, predicted in 1965 that the continued develop of silicon chips will force the amount of transistors in those chips to double every two years\(^1\). Remarkably, that prediction has come out to be fairly accurate. As a result, the necessary cooling rates are less than adequate in modern electronics with the amount of transistors now exceeding 2 billion in a 2.2 square
centimeter silicon Pentium microprocessor. In parallel with the increased number of transistors, the device themselves are getting increasingly smaller, causing a serious issue in incorporating cooling techniques for the electronics. Typical silicon chips, or “dies,” operating at 85°C can experience heat fluxes upwards of 100W/cm\(^2\) and centralized hotspots reaching 1 kW/cm\(^2\). With the current direction that innovative companies are headed with smaller packages and faster processing speeds, thermal management is top priority and a major concern for the future of these electronic devices.

A technological advancement that has spawned from the thermal management bottleneck is the utilization of multiple core processors to help control excess heat production, among other reasons. In order to control hot spots on individual computer chips, the multiple cores work together in a particular architecture where certain chips are turned off at strategic times to mitigate excess heat. While companies have now gone to triple and even quad core processors, thermal management is still a major concern in the design of such devices.

### 1.1.2. Air Force Applications

Air Force integrated devices have long been experiencing thermal management issues due to the motivation for high power components that meet strict military requirements for weight, size, and design. In order to keep up with the demand for future “sixth generation” fighters, a significantly different approach to design of subsystems in needed. Newly crafted F-35 fighters generate heat loads exceeding 300 kW and F-22 fighters are now surpassing 600 kW in cruising conditions. Excess heat produced that is uncontrollable by commonly used cooling techniques is typically absorbed by the fuel and rejected through the engine. The fighters are currently maxed
out in heat mitigation using the outdated cooling techniques, and the current fear of overheating circuit components and causing havoc to high heat flux producing systems is increasingly evident. The potential for the addition of high-energy laser weapons systems has increased the cooling requirements to the megawatts class of total thermal load. A representation of thermal loads experienced in typical Air Force applications both past, present, and future are displayed in Figure 1.

![Figure 1: Thermal loads experienced in various Air Force technologies](image)

Another major issue with current heat mitigation schemes used for the military is that the technologies are required to be designed for peak power or “worst case scenario.” Overheating of these new aircraft occurs more often while the aircraft is running and operating on the ground, where it is more difficult to cool. An optimal system would include a design for dynamic cooling capability changes based on the heat load and temperatures at any given time. These new systems could benefit the military by
reducing the need for large, complex, heavy cooling systems and replacing them with active cooling schemes. Targets set out by the Air Force Research Laboratory (AFRL) include a fivefold increase in cooling capacity while cutting both the weight and volume in half.

1.2. Cooling Techniques

Techniques incorporating natural convection via a metal heat sink, forced convection involving a fan or a water cooling system have long been used as primary cooling methods for computer chips and other devices. Mudawar\textsuperscript{5} discusses the differences between these techniques for use in high heat flux thermal management schemes. Referenced throughout the scientific community as an inherent motivation to incorporate boiling heat transfer into these high heat flux systems, Figure 2 displays the heat transfer coefficient (HTC) associated with certain types of cooling schemes using different fluids. The heat transfer coefficient is typically expressed in terms of the amount of heat flux per unit temperature (W/cm\textsuperscript{2}·°C).
Figure 2: Heat transfer coefficients attainable with natural convection, single-phase forced convection, and boiling for air, fluorochemical liquids, and water.  

The techniques displayed in Figure 2 give a broad overview of the heat transfer capabilities for three fluids: air, fluorochemical liquids, and water. Air is the most widely used fluid of choice due to the ease of availability, and most common cooling fluid utilized in electronics. Air cooling using a natural convection scheme involves the heated chip attached to some sort of highly thermally conductive heat sink. This acts as a thermal reservoir and increases interfacial surface area to increase the rate of heat transfer away from the chip. As the air heats up around the heat sink, buoyancy forces drive the air upwards forcing cooler air to come closer in contact with the surface. Single-phase forced convection utilizing air as the working fluid provides an approximate order of magnitude increase in the rate of heat dissipation from natural convection. A use of a fan or some type of blower to circulate air over the heated die increases the rate of cooler air to the surface, instead of relying on buoyancy forces. These two methods are typically
used in parallel in the same processing unit. Although this can provide sufficient cooling for certain applications, poor thermal transport properties of air limit the use for high heat flux technologies.  

Improved thermal transport opportunities can be realized with direct or indirect liquid contact with the hot surface. Natural and single-phase forced convection cooling using liquids with high thermal conductivity, low viscosity, and high specific heat can lead to significantly higher cooling rates. In natural convection under direct immersion conditions, the cooling is done by convective movement of the hot liquid upwards and causing the subsequent cooler liquid downwards towards the surface. Although this is a very simple cooling technique and easy to implement, it is limited by how quickly the cooler fluid can flow down towards the hot surface. This velocity is critical in determining cooling rates and is a function of the temperature gradient within the pool, liquid viscosity, and density.

Forced convection cooling using water, other thermally stable liquids, and fluorochemicals is very effective for cooling electronics, and involves a much more complex, space-consuming system. A system with pumps and flow controllers complicates the cooling process. However, new technologies in electronics necessitate complete redesign of thermal management systems to accommodate new demands in heat dissipation. Air Force applications have specific requirements that can be different from commercial uses. One example of an application that utilizes a forced convective cooling system is for the Radar Array power supply in the F-18 Fighter. The liquid supplied in the forced convective cooling system is polyalphaolephin (PAO). PAO is polymer with a single alkene monomer that starts at the alpha carbon atom and branches a long chained
alkane from the gamma carbon. PAO has poor thermal performance, but has other favorable properties such as remaining a liquid at a large temperature range and retaining a relatively low viscosity at lower temperatures.

Liquid to vapor phase change processes have several advantages that make them highly advantageous in cooling applications including high heat transfer coefficients and a nearly isothermal heat transfer. As shown in Figure 2, boiling of both fluorochemical liquids and water can achieve orders of magnitude better heat transfer coefficients than the previously discussed cooling methods. These techniques will be discussed in subsequent sections.

1.2.1. Boiling

Efficient thermal energy conversion from boiling can be traced to the large changes in enthalpy, entropy, and volume during the liquid-vapor phase transition process\(^8\). As bubbles nucleate and expel from a heated surface, both the convective and phase change heat transfer components contribute to an overall heat transfer that is much greater than convection alone. The amount of heat absorbed or expelled by an entity undergoing a phase transition at a constant temperature is known as the latent heat\(^9\). Specifically, the latent heat of vaporization refers to a phase transition from liquid to vapor. The latent heat is a fundamental physical property of a fluid and is a measure as to how much energy per unit mass released or absorbed by a fluid undergoing either evaporation or condensation.
1.2.1.1. Typical Fluids Used in Phase Change Systems

Determining the appropriate fluid for a boiling heat transfer application depends on many of the system conditions such as device temperatures, pressures, flow rate (if applicable), and cooling requirements. Fluorochemical liquids such as FC-72, FC-87, and PF-5052 are typically composed of specific arrangements of carbon, hydrogen, and fluorine and are widely studied for use in boiling heat transfer applications\textsuperscript{10-12}. They exhibit lower boiling temperatures than water, which makes them advantageous to use for maintaining a lower device temperature. These “refrigerants” are renowned for low saturation temperatures while maintaining the benefits of a low viscosity comparable to water. However, thermal properties of dielectric coolants such as specific heat, both liquid and vapor density, and latent heat are inferior to water. One major issue plaguing many of these refrigerants and prohibiting their use in certain applications is their environmental impact. There is a continued effort to attempt to maintain advantageous thermal properties while minimizing the Ozone Depletion Potential (ODP) and Global Warming Potential (GWP). Water is also readily used due to its advantageous thermal properties for boiling heat transfer. The major disadvantages with using water in a boiling heat transfer application are the high saturation temperature and electrical compatibility requirements where water cannot come in direct contact with the sensitive components in the system\textsuperscript{5}. Despite these disadvantages, the extremely high latent heat, specific heat, and volume change during boiling make water a very valuable, and as a result, highly utilized boiling fluid. Table 1 displays the critical properties of commonly used boiling fluids.
Table 1: Thermophysical properties of typical boiling fluids of interest

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Saturation temperature $T_{sat}$ (°C)</th>
<th>Liquid density $\rho_f$ (kg m$^{-3}$)</th>
<th>Liquid specific heat $c_p, f$ (J kg$^{-1}$ K$^{-1}$)</th>
<th>Vapor density $\rho_g$ (kg m$^{-3}$)</th>
<th>Latent heat of vaporization $h_{fg}$ (kJ kg$^{-1}$)</th>
<th>Surface tension $\sigma \times 10^3$ (N m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC-72</td>
<td>56.6</td>
<td>1600.1</td>
<td>1102.0</td>
<td>13.43</td>
<td>94.8</td>
<td>8.35</td>
</tr>
<tr>
<td>FC-87</td>
<td>32.0</td>
<td>1595.0</td>
<td>1060.0</td>
<td>13.65</td>
<td>87.93</td>
<td>14.53</td>
</tr>
<tr>
<td>PF-5052</td>
<td>50.0</td>
<td>1643.2</td>
<td>936.3</td>
<td>11.98</td>
<td>104.7</td>
<td>13.00</td>
</tr>
<tr>
<td>Water</td>
<td>100.0</td>
<td>957.9</td>
<td>4217.0</td>
<td>0.60</td>
<td>2256.7</td>
<td>58.91</td>
</tr>
</tbody>
</table>

1.3. Pool Boiling

Boiling on a surface of a body submerged in a semi-infinite, motionless liquid pool is known as pool boiling. Practical examples of pool boiling are quenching of metallurgical processes$^{13}$, cooling of electronic components via immersion$^{14}$, vapor compression systems$^{15}$, and many others. A thermosyphon is a commonly used pool boiling cooling device, and two examples of thermosyphons are seen in Figure 3. The thermosyphon removes heat by producing vapor bubbles on the surface that are driven off by buoyancy forces. The upper region of the container has a condenser which re-condenses the vapor back to the liquid form where it returns to the stagnant pool.

Advantages to this cooling technique include the use of passive circulation, ease of fabrication, and the ability to use phase change to dissipate high heat fluxes$^5$. The process that is used for thermosyphons and any pool boiling technique is strongly dependent on multiple properties such as the thermophysical properties of the liquid and vapor, the surface material preparation and thermal properties, and the design of the apparatus itself including size of the heated surface and boundary conditions$^9$. 
Figure 3: a) Air-cooled thermosyphon for a single processor and b) multiple processor thermosyphon

1.3.1. Boiling Mechanisms

The study of nucleate boiling involves numerous processes and subprocesses closely linked and interacting in a complex manner. Vapor bubbles are generated at the heating surface, rise through the liquid bulk, and disengage from the surface of the liquid. Three aspects considered in this process are the liquid, the heated wall, and the liquid-
wall interface. Figure 4 highlights the nonlinear interactions between these three distinct areas. The most important and complex of these areas in nucleate boiling studies fall under the liquid-wall interaction, and are represented inside of the dotted line of Figure 4. Issues involving contact angle, nucleation-site density, and surface characteristics will be closely examined in future sections.

Figure 4: Conjugate non-linear complexities of boiling

Upon bubble formation and departure from a heated surface, both thermal and hydrodynamic interactions govern the boiling characteristics. Figure 5 highlights four distinct interconnections between the heated surface and liquid bulk. Interactions 1 and 3, i.e. thermal interaction between the heated surface and bubble and hydrodynamic interaction between the bubble and liquid bulk, are considered as auto-interactions at a single nucleation site. The complexity of boiling research primarily stems from interactions 2 and 4, where two adjacent nucleation sites interact thermally and the
hydrodynamic interaction between two separate bubbles arising from adjacent nucleation site feel the presence of the other.

![Diagram of bubble interactions](image)

**Figure 5: Thermal and hydrodynamic interactions of bubble formation and departure on a heated surface**

In boiling, the main heat transfer mechanisms can be simplified to: transient conduction into the liquid adjacent to the wall, microlayer evaporation underneath the bubbles, and natural convection on the inactive area of the heater. The overall heat transfer is a summation of these individual heat transfer mechanisms. Convective heat transfer includes free convection, forced convection due to the motion of bubble growth, and convection when the bulk liquid fills the space of a departed bubble. Experimental data has shown that evaporation is the dominant mechanism and that the maximum amount of energy is removed directly from phase change phenomena occurring on the heated surface.
1.3.2. Pool Boiling Research

Pool boiling is not only an effective heat transfer scheme, but is a commonly employed technique used to characterize multiphase heat transfer properties of both specifically engineered surfaces and liquid to vapor phase change coolants. Experiments are performed by submerging a sample of interest into a body of liquid essentially at rest, where the motion of the boiling vapor is due to natural convection conditions. Buoyancy forces caused by large density differences between the liquid and vapor states drive vapor away from the surface and subsequent liquid down to the hot surface.

A saturated pool boiling characterization curve for a horizontal plate or thin metal wire is displayed in Figure 6. This curve classically interprets pool boiling data and stems back from early works of Nukiyama\textsuperscript{19}, Jacob and Linke\textsuperscript{20}, and others. The heat flux is plotted with respect to the temperature difference between the surface and the saturation temperature of the liquid at the given conditions. The slope of the curve at any given point along the curve is the heat transfer coefficient, $h$, found in Newton’s Law of Cooling expression for this particular system:

$$q_s = h \cdot (T_{\text{sur}} - T_{\text{sat}})$$  \hspace{1cm} (1)

where $q_s$ is the heat flux at the substrate surface (W/cm\textsuperscript{2}), $h$ is the heat transfer coefficient (W/cm\textsuperscript{2}.°C), and $T_{\text{sur}} - T_{\text{sat}}$ is the difference between the surface temperature and the saturation temperature of the boiling fluid.
The boiling curve can be broken up into the following five unique regimes referred to as natural convection, partial nucleate boiling, fully developed nucleate boiling, unstable film boiling, and stable film boiling. By evaluating the heat transfer behavior of the fluid-solid interface at each regime individually, a better insight into fundamental phenomena can be obtained. Experimental data is generated by increasing the wall superheat and heat flux slowly in the nucleate boiling regime and measuring the heat flux and superheat at steady state conditions.

At low superheat temperatures, the dominating mechanism for heat transfer is due to natural convection. The surface temperature will be slightly higher than that of the pool of liquid, and not sufficient to nucleate any bubbles on the substrate. As the fluid comes in contact or near the slightly hotter surface, the convective heating forces the
liquid upwards due to the buoyancy differences of the hotter liquid and the lower temperature liquid away from the source. Figure 7 gives a pictorial representation of the natural convective flow on a heated substrate.

![Figure 7: Convective flow patterns on a heated substrate where $T_{sur}>T_{pool}$](image)

The nucleate boiling regime is first realized as the heat input to the system increases and the wall superheat reaches a certain value where vapor bubbles begin to appear on the surface. The isolated bubble regime initiates at this point, known as the onset of nucleate boiling (ONB). Vapor bubbles tend to first form on defects or cavities in the surface that contain a pre-existing gas/vapor nuclei\textsuperscript{17}. These vapor bubbles nucleate in and release from random active sites throughout the surface and do not interact with one another until released away from the heated substrate. The frequency and relative density of the isolated bubbles, along with the velocity of release, increases with wall superheat. Due to the increased heat transfer rate associated with bubble formation, the heat transfer coefficient at that point begins to increase, as evident in point A in Figure 6.

Fully developed nucleate boiling begins when the wall temperature increases the number of active sites to where adjacent sites merge together quickly to form slugs or
columns of vapor. The vapor rises rapidly and violently upwards towards the top of the semi-infinite pool of liquid. Bubbles form and quickly coalesce to form vapor structures that appear to look like mushrooms with several stems. The heat transfer coefficient (HTC), represented from point B to C in Figure 6, is the maximum heat transfer rate of a particular surface-fluid combination under boiling conditions.

As the wall superheat and heat flux within the fully developed nucleate boiling regime continue to increase, the flow of liquid replenishment to the surface is significantly decreased. Helmholtz instabilities begin to occur where vapor jets are distorted and thus block liquid flow towards the heated surface. The vapor drag on the liquid moving towards the surface causes this decrease in replenishment rate and eventually leads to a critical point where the surface cannot be completely wetted with liquid. An example of this Helmholtz instability of an interface is seen in Figure 8. The roll-over and eventual peak in the heat flux is known as the critical heat flux (CHF), and is represented in Figure 6 as point C. The CHF condition is a practical limitation for heat transfer applications in that a blanket of vapor forms over the surface as the curve enters the transition boiling regime. Due to the low thermal conductivity of the vapor in comparison to the liquid, the heat flux drops significantly and a large temperature increase occurs. For instance, the nucleate boiling regime typically occurs when the surface superheat is anywhere from 7°C-25°C, where post-CHF temperature can increase to 200°C in a matter of seconds. The critical heat flux term indicates the upper limit of nucleate boiling, and exceeding this heat flux in a practical application can lead to devastating effects.
Once the peak heat flux is reached, transition boiling, or unstable film boiling, begins and is represented by the regime from point C to point D in Figure 6. This regime is characterized by a decrease in the overall mean heat flux with large increases in temperature. The vapor film formed after the critical heat flux is unstable, inducing rapid and severe fluctuations in both the local surface temperature and local surface heat flux. These fluctuations are present due to unstable dry regions on the surface, which exist only for a short amount of time before collapsing and allowing rewetting of the surface\textsuperscript{9}. The release of bubbles in this regime has been considered to emulate explosions of vapor away from the surface\textsuperscript{22}. Unstable film boiling occurs for several seconds until the minimum heat flux (MHF) is reached, represented by point D in Figure 6. Numerous studies have been conducted just on this region alone, with still some debate on the distinct fundamental mechanisms behind the unstable film regime\textsuperscript{23,24}.

Once the surface is at a high enough temperature to sustain a stable vapor film, the minimum heat flux is reached and the heat transfer coefficient begins to increase.
again. This regime is known as stable film boiling. In the stable film boiling regime, the heat flux increases as a consequence of the increased conduction and convection due to a larger driving temperature difference between the liquid and surface. At increasing temperatures, radiation becomes the dominant transport across the vapor layer. Vapor bubbles release from the substrate at a certain frequency governed by the Taylor instability wavelength. The Taylor instability phenomena occurs at an interface between two fluids at different densities where the light fluid is pushing up on the heavier fluid. The instability of the lighter fluid causes formation of wavy interfaces which lead to a slow release of vapor bubbles at a rate of orders of magnitude less than in nucleate boiling. The stability of the film increases and release of the bubbles during film boiling decrease as the heat flux and wall superheat increase. Film boiling will continue to occur as the temperature increases and is only bound by system limitations and materials capabilities.

The three most important parameters for pool boiling characterization are the onset of nucleate boiling (ONB), heat transfer coefficient (HTC), and critical heat flux (CHF). They are each interrelated and optimizing the ONB, HTC, and CHF simultaneously is a difficult achievement. Each of these parameters is strongly dependent upon a multitude of factors such as surface roughness, contact angle, and fluid properties and will be discussed in the succeeding sections more in detail.

1.3.3. Surface Engineering

Surface roughness is the most important factor affecting the boiling heat transfer results primarily because it increases surface area and directly influences nucleation site density. Most surface engineering can be lumped into three critical categories, as
explained by Chen\textsuperscript{8}. The first, and most broad, category involves surface modification by increasing surface roughness\textsuperscript{26-28}, coating with some sort of micro or nanostructures\textsuperscript{29-31}, or using nanofluids as a means to deposit nanoparticles on the surface\textsuperscript{32,33}. The second means of surface modification involves formation of microfabricated pin-fin structures to increase heat transfer surface area\textsuperscript{34,35}. These fabricated pin-fin structures are typically cylindrical rods on the order of several micrometers in diameter up to a millimeter in some cases. The third method of surface modification to improve boiling heat transfer is to employ some sort of wicking structure to increase liquid flow to the surface by capillary pumping\textsuperscript{36-38}. The porous structures tend to delay the CHF point by increasing capillary forces and delaying the occurrence of the hydrodynamic instability, thus increasing the CHF value.

Several studies have been conducted recently where values of CHF and HTC were enhanced using alternating hydrophobic/hydrophilic surface architecture. For example, Betz measured the pool boiling properties of oxidized silicon wafer substrates with patterned wettabilities. The sample was composed of 40 μm hexagons of hydrophobic fluoropolymer film (contact angle 110°) on a hydrophilic silicon dioxide surface (contact angle <25°C), and improved both boiling parameters simultaneously\textsuperscript{39}.

New technologies in nanowire synthesis have led the boiling community to expand the typical methodology to include a new class of surface engineering. Nanowires have been observed to contain orders of magnitude increase in cavities and pores as compared to microfabrication methods, contain a much higher effective heat transfer area, and may also act as an efficient wicking structure initiating large capillary forces\textsuperscript{8}. The combination of all of these attributes leads nanowires to be of extreme
interest for increasing both CHF and HTC simultaneously, which is very difficult in other surface engineering techniques.

1.3.4. Surface Energy

The affinity of liquids for solids is referred to as the wettability of the fluid and is also referred to as the surface energy\(^9\). Surface energy is a major component in the fluid-wall interfacial properties and has a strong affect on boiling performance. The wettability of a fluid is typically determined by placing a droplet of liquid on a substrate of interest and measuring the angle of the liquid-vapor-solid interface. The angle itself is a mixture of the contribution of three interfacial forces and is expressed using the Young’s equation:

\[
\sigma_S = \sigma_{SL} + \sigma_L \cos \theta
\]  

where \(\sigma_S\) is the surface tension of the solid, \(\sigma_L\) is the surface tension of the liquid, and \(\sigma_{SL}\) the interfacial tension between the solid and liquid. The contact angle is on a smooth surface at room temperature and is represented as \(\theta\). At contact angles above 90°, the surface is considered hydrophobic and is characterized as having poor adhesiveness, poor wettability, and low surface energy. In contrast, a hydrophilic surface exhibits a contact angle of less than 90° and the liquid wets the surface and shows good adhesion.

The importance of using a smooth, repeatable surface for both contact angle and boiling experiments is evident in research conducted by Onda\(^40\). On already hydrophilic surfaces, roughening of the substrate leads to increased wicking through the roughness features, leading to a decrease in contact angle. Likewise, an increase of roughness on an already hydrophobic sample will cause pinning of the contact angle on the roughness features. This phenomenon can be seen in Figure 9.
Boiling results are also strongly dependent on the surface contact angle\textsuperscript{16}. Hydrophobic surfaces cause bubbles to form at low heat flux and surface temperature, which can also lead to a higher heat transfer coefficient especially in the isolated bubble regime. The strongly hydrophilic surfaces will wick the fluid horizontally and allow for more “wetting” of the surface. This tends to directly result in a delay in the ONB temperature and also delay the formation of a vapor layer at CHF. Many boiling studies concerned with surface wettability and the affect on CHF have been performed and show an increase in CHF with an increase in wettability\textsuperscript{32,41,42}. A typical hydrophilic and hydrophobic boiling curve on a smooth surface is shown in Figure 10, with the arrows signifying CHF condition and a rapid increase in temperature.

\textbf{Figure 9: Effect of surface roughness on contact angle}
Figure 10: Typical hydrophobic and hydrophilic pool boiling curves on a smooth surface

A nanoengineered surface can potentially behave differently than a smooth surface in terms of ONB temperature, HTC, and CHF. For example, carbon nanotubes have shown to decrease the ONB temperature and increase HTC with an increase in hydrophilicity\(^43\). This phenomenon will be discussed in a later section.

### 1.3.5. Active Thermal Control

Active control of heat transfer processes are desirable in current devices due to irregularities in the system environment, changing power loads, potential to reduce energy consumption, and the need to simplify cooling systems\(^43\). Attempts have been made to utilize outside stimuli to enhance and control various boiling mechanisms during the boiling process. For instance, Park uses ultrasonic vibrations to delay the formation of a continuous vapor layer\(^44\). More recently, advances in control of boiling heat transfer have been realized using photonic excitement of surfaces.
1.3.6. Photoactive Surfaces

The possibility of surface wettability changes due to light exposure have led to a significant interest for active thermal control during boiling and evaporation processes. A multitude of molecular structures have the ability to alter their surface wettability upon exposure to light including certain azobenzenes\textsuperscript{45}, transition metal oxides such as titanium dioxide, and other photocatalysts.

1.3.6.1. Copper and Copper Oxides

Copper has a vast history of applications involving heat transfer. The high thermal conductivity (400W/m·K), high electrical conductivity, ease of manufacture, and cost make it an ideal metal to use in heat exchangers, evaporators, and other modes of heat dissipation. Pool boiling studies have long been performed on copper to determine the critical parameters such as heat transfer coefficient, critical heat flux, and onset of nucleate boiling. The testing of pure copper under UV-irradiation and boiling conditions hasn’t been fully investigated.

Numerous photocatalytic investigations have been performed with copper oxides incorporated within a transition metal oxide matrix\textsuperscript{46-49}. The photophysical properties vary depending upon which oxidation state of copper on the surface. Copper (I) oxide, or cuprous oxide Cu\textsubscript{2}O, and Copper (II) oxide, or cupric oxide CuO, vary in both stability, absorption, and other critical properties. CuO, is a p-type semiconductor with a narrow band gap of 1.2 eV. Cu\textsubscript{2}O, is also a p-type semiconductor but with a larger band gap energy of 2.2 eV. One investigation discovered that the hybridization of the two copper oxide species led to a higher photocatalytic activity than the single species alone\textsuperscript{50}. 
A clear understanding of surface chemistry during boiling experiments is imperative to understanding the effect that UV irradiation has on copper and the different copper oxide states. Difficulties arise in studying these types of samples in boiling tests because two different oxidation mechanisms are in effect: corrosion and oxidation acceleration due to high temperatures, and that caused by UV light.

1.3.6.2. Titanium Dioxide

Titanium dioxide is a very attractive photocatalyst due to its strong oxidizing power under UV irradiation, leading to advantageous anti-fouling tendencies\textsuperscript{51} coupled with the ability to become superhydrophobic upon light exposure\textsuperscript{52}. Titanium dioxide is normally hydrophilic but becomes superhydrophilic upon irradiation. The contact angle of water on an irradiated titanium dioxide surface decreases with time and eventually reaches a value very close to zero. Because of the significant change in contact angle, TiO\textsubscript{2} is potentially useful for actively controlling boiling applications\textsuperscript{53}.

The mechanism for this superhydrophilic transformation is presented by Hashimoto\textsuperscript{54}. Photogenerated holes are responsible for the superhydrophilic conversion. A schematic illustration in Figure 11 depicts how the trapped holes may react with TiO\textsubscript{2} and break the bond between the lattice metal oxide by the coordination of water molecules at the titanium site. Upon UV irradiation, coordinated water molecules release a proton for charge compensation, allowing for an additional OH\textsuperscript{−} group to form. The surface energy decreases because the singly coordinated new OH\textsuperscript{−} groups are less stable than the initial doubly coordinated OH\textsuperscript{−} groups. Thus, the surface energy of the film covered with thermodynamically less stable OH\textsuperscript{−} groups is higher than the titanium
dioxide surface with just the initial OH\textsuperscript{-} group attachment. The water droplet then spreads completely over the surface similar to a two-dimensional capillary flow.

![Diagram of reversible changes in amount of hydroxyl groups on TiO\textsubscript{2} film under UV light irradiation](image)

**Figure 11:** Illustration of reversible changes in amount of hydroxyl groups on TiO\textsubscript{2} film under UV light irradiation\textsuperscript{54}

Contact angle studies have been performed on these films, with the resulting angle approaching zero after several hours of light irradiation. Studies by Takata\textsuperscript{53} are displayed below in Figure 12. The contact angle decreases significantly with light exposure, but requires several hours of irradiation time. Likewise, the reversion time back to the initial somewhat hydrophobic state takes hundreds of hours to occur.

Timescales for this switch are quite long, especially for applications that require rapid change in cooling rates. A device using these types of surfaces would likely need to contain a hybridized surface with increasing nanoscale roughness features, or another method to speed up the surface energy switching time.
For pool boiling heat transfer applications with active control, titanium dioxide provides the necessary change in surface energy that has the potential to impact boiling performance. A mechanistic study to examine pool boiling results of smooth titanium dioxide films can provide helpful information on transition metal oxide photocatalytic activity under UV-irradiated boiling.

**1.3.6.3. Carbon Nanotubes**

Carbon nanotubes (CNTs) are renowned for their extremely advantageous thermal and mechanical properties especially their high axial thermal conductivity, electrical conductivity, and tensile strength. Arrays of CNTs have also shown promise in boiling applications by providing cavities that are extremely effective in reducing superheat and increasing heat transfer rates during nucleate boiling. The CNT mesh provides these “reservoir-type” cavities that are able to initiate and sustain boiling heat transfer. However, one disadvantage of using multi-walled CNT arrays for boiling surfaces is that
they are inherently hydrophobic. Recent investigations have shown that multi-walled CNT arrays exhibit a reversible hydrophobic to hydrophilic behavior upon exposure to UV light\textsuperscript{57}. Moreover, the exposure time for conversion is much less than typical metal oxide photocatalysts.

Potential mechanisms for the superhydrophilic conversion of CNTs exposed to UV irradiation follow very closely to those of transition metal oxides. The formation of an electron-hole pair at the CNT interface attracts hydroxyl groups and increases hydrogen bonding at the lattice defects of CNTs, yielding a more hydrophilic film. Once the UV irradiated film is placed in the dark, the hydroxyl containing water molecules absorbed to the surface are gradually replaced by oxygen molecules, causing the CNT film to become more hydrophobic. Oxygen adsorption is more thermodynamically favored and is more strongly bonded to the defect sites than water\textsuperscript{58,59}. Studies performed by Yang also indicate a change in the X-Ray Photoelectron Spectroscopy (XPS) O 1s peak before and after irradiation on CNT samples, indicating a higher concentration of hydroxyl groups and water trapped within the CNT matrix\textsuperscript{57}. An illustration of the mechanism for hydrophilic conversion of CNTs with UV irradiation along with an XPS high resolution scan is seen in Figure 13.
Previous flow boiling experiments using UV irradiation have been performed on multi-walled CNT arrays to determine the change in critical parameters associated with flow boiling. Kousalya\textsuperscript{43} was able to achieve an effective HTC change of approximately 41.5% with a decrease in incipience boiling temperature of 4.6°C with 48 hours of UV-irradiation using an LED light with an optical energy around 83 mW/cm\textsuperscript{2}. He also noted that the boiling curve partially reverts to the pre-irradiated position once the samples were placed in darkness for several hours. Overall, Kousalya observed that the CNT-coated surfaces can be photonically excited and result in significant changes in ONB temperature and an increase in HTC. As seen in Figure 14, a clear change in boiling performance parameters such as HTC and ONB point was observed. A pool boiling investigation of CNT arrays could corroborate these mechanisms and provide additional insights into how CNT arrays respond to UV-irradiation.
1.3.7. Modeling

Physical models have been used to gain a fundamental understanding of transport properties during nucleate pool boiling. Attempts have been made to create an all-inclusive model, but in most instances the models only work well for very specific conditions. Several important models to describe aspects of boiling are covered in the following sections. Rohsenhow’s model for heat transfer coefficients can be seen in Appendix A.

1.3.7.1. Zuber Model for Critical Heat Flux

Zuber’s model for CHF has been utilized specifically in cases of large heater sizes to determine a rough critical heat flux approximation. His theory is based upon the influence of both Taylor wavelength and Helmholtz instabilities on liquid replenishment rate to the substrate. The expression for the critical Taylor Wavelength of instability is seen below:
\[
\lambda_T = 2\pi \left[ \frac{\sigma}{g(\rho_l-\rho_v)} \right]^{1/2}
\]  

(3)

where \(\lambda_T\) is the wavelength of Taylor instability, \(\sigma\) is the liquid surface tension, \(g\) is the gravitational constant, and \(\rho_l\) and \(\rho_v\) are the liquid and vapor densities, respectively. For a steam-water system at 100°C, the value for Taylor wavelength of instability is about 1.6 cm. Therefore, only perturbations having the wavelengths greater than 1.6 cm will lead to instability of the interface. Zuber used this expression in his analysis and his prediction of CHF resulted in the expression

\[
q''_{CHF} = C h_{lv} \rho_v \left[ \frac{\sigma g (\rho_l-\rho_v)}{\rho_v^2} \right]^{1/4}
\]

(4)

where \(h_{lv}\) is the latent heat of vaporization, and \(q''_{CHF}\) is the critical heat flux value. The constant \(C\) was proposed by Zuber to have a value of 0.131, and was confirmed by Kutateladze using empirical correlations to be a good fit for prediction of CHF. An infinite surface model proposed by Lienhard and Dhir yielded a value of \(C=0.149\), but a value of 0.131 was recommended for practical systems under the influence of boundary conditions.

The major criticism of the Zuber/Kutateladze model is that it does not take into account the effects of the geometry, surface condition, and wetting characteristics of the heater surface. Experimental data at the time for wettability was not available and limitations to technology made it impossible to separate these effects, and so this model is generally used as a first step approach.
1.3.7.2. Kandlikar’s Model for Critical Heat Flux

Kandlikar’s model proposed in 2001, decades later than Zuber, applied a set of force balances at the moment of departure of a bubble\textsuperscript{62}. Importantly, it included the effects of surface wettability and heater orientation on the CHF condition. The analysis began with a force balance parallel to the heater surface on a bubble just prior to departure, as depicted in Figure 15.

![Figure 15: Forces due to surface tension, gravity, and momentum acting parallel to the heater surface on a bubble\textsuperscript{62}](image)

Surface tension forces $F_{S,2}$ and $F_{S,1}$ act at the bubble top surface and base, respectively. The hydraulic pressure gradient due to gravity results in a triangular pressure distribution with $F_G$ as the resultant force. At high evaporation rates the force due to change in momentum, $F_M$, due to evaporation causes the liquid-vapor interface to move rapidly along the heater, thus initiating a vapor blanket. Therefore, at the inception of the CHF condition, the force balance yields

$$F_M = F_{S,1} + F_{S,2} + F_G$$ \hspace{1cm} (5)

By doing a force balance at the departure conditions, and factoring in some hydrodynamic theory using the Taylor wavelength of instability similar to that in Zuber’s
analysis, a form of the force balance incorporating contact angle and heater orientation
can be formulated to predict the CHF

\[ q_{\text{CHF}}^* = h_l \rho_g \sqrt{\frac{1 + \cos \beta}{16}} \left[ \frac{\pi}{2} + \frac{\pi}{4} (1 + \cos \beta) \cos \phi \right]^{1/2} \left[ \sigma g (\rho_l - \rho_v) \right]^{1/4} \]  

(6)

where \( \beta \) is the dynamic receding contact angle and \( \phi \) is the heater orientation (0° for
horizontal heaters). A graph of Kandlikar’s prediction method for water on a horizontal
surface is seen in Figure 16.

![Figure 16: Kandlikar’s model CHF prediction for varying contact angles of water
on a horizontal heater](image)

The model suggests that a significant contribution to the CHF condition stems
from the contact angle of the fluid with the heater. Large changes in CHF are exhibited
at modest contact angles, where smaller change in CHF is observed at the extremes.
Overall, the effects of contact angle changes upon CHF are well accounted for in
Kandlikar’s model.
1.3.8. Characterization Instruments

Pool boiling experimental apparatuses typically include temperature and heat flux measurements, along with optical techniques in some studies to characterize bubble dynamics and liquid-vapor interfacial properties\textsuperscript{63,64}. Thermocouples are used to measure surface temperature via direct measurement, or Fourier’s Law of heat conduction is used to extrapolate the surface temperature based on temperature below the surface and the heat flux. Heat flux is either determined by a set of thermocouples underneath the substrate or by taking the heater power used and assuming a certain heat loss. Either method is represented well in the boiling community and are both practiced often to measure heat flux.

Optical techniques have long been utilized as a means to gathering information regarding bubble size, departure speed, and other interfacial characteristics. As early as 1955, Westwater was able to take both video and still images of the of pool boiling on a heated wire\textsuperscript{63}. He was able to take 4000 frames per second video that required a 100 foot reel of 16-mm film to be passed through every second. Because of his studies, researchers were able to gain insight on bubble frequency generation and departure velocities. He determined that during nucleate boiling, the time for one bubble to grow and depart is 0.059 seconds on average, and that the frequency of bubble generation and departure was around 17 per second. Researchers continue to perform optical characterization during pool boiling studies to gain insightful knowledge of liquid-vapor phenomena.

Additional methods to characterize liquid-vapor phase change processes could potentially aid in the understanding of fundamental boiling processes. A method that
could have a significant impact on measuring the overall liquid-solid contact and important boiling characteristics is Electrochemical Impedance Spectroscopy (EIS).

1.3.9. Electrochemical Impedance Spectroscopy

Electrochemical techniques have long been used to investigate surface degradation due to corrosion by measurement of corrosion rate at a nearly instantaneous point\(^6\). The mechanism behind corrosive attack in solid-liquid systems lies at the solid-electrolyte interface. By mapping anodic and cathodic processes of ion and electron flow at that interface of the material, an accurate corrosion rate can be evaluated in a very short time frame. A need to control and study corrosion rates in different environments is ever present and necessary for engineers to ensure optimal functioning of materials in terms of safety and economic aspects\(^6\).

Corrosion prediction and control can be evaluated using electrochemical impedance measurements. Electrochemical impedance is a physical representation of the opposition to an alternating current (AC) in an electrical system and comprises of both resistive and capacitive elements to an electrical current. Ohm’s law, modified for the case of a non-zero frequency, is defined as \( E(\omega) = I(\omega) \times Z(\omega) \), where \( E \), \( I \), and \( Z \) are the complex voltage, current, and impedance, and are unique to a given frequency \( \omega \). The complex electrical impedance, \( Z \), incorporates both a real component, \( Z' \), and an imaginary component, \( Z'' \). The vector representation of the impedance has magnitude \( |Z| \) and can be calculated from the following expression\(^6\):

\[
|Z| = \sqrt{(Z')^2 + (Z'')^2} \tag{7}
\]

One particular means by which corrosion protection systems are evaluated is using a technique known as Electrochemical Impedance Spectroscopy (EIS). Impedance
is monitored over a large frequency range, where low frequency impedance is related to the corrosion activity on the metal surface, and the high frequency part of the spectrum is related to the barrier properties of the coating itself \(^{68}\). By fitting the impedance data to a physical circuit model that incorporates resistive and capacitive elements, insights to the physical phenomena can be gained. The impedance of each of these circuit elements is expressed below:

\[
\text{Resistor: } Z_R = R \tag{8}
\]

\[
\text{Capacitor: } Z_C = \frac{1}{i\omega C} \quad \text{where: } i = \sqrt{-1}
\]

\[
\omega = \text{angular frequency} \left( \frac{\text{rad}}{s} \right)
\]

\[
C = \text{Capacitance (F)}
\]

The phase angle, \(\theta\), represents the offset of the current response to the voltage. A phase angle of 0 degrees indicates a purely resistive circuit with a zero imaginary impedance component and an angle of -90 degrees indicates a purely capacitance contribution to the impedance. The expression for calculating the phase angle can be seen below:

\[
\theta_p = \tan^{-1}\left( \frac{Z''}{Z'} \right) \tag{9}
\]

By monitoring the changes to these fundamental properties within the corrosion system in terms of their circuit elements, a powerful insight can be achieved through a simple electrochemical technique.

An electrochemical impedance technique utilized frequently in multiphase flow systems is known as Electrochemical Impedance Tomography (EIT) \(^{69}\). The EIT technique isolates the different electrical impedances of the multiple phases in flow to create a physical flow map. By implementing numerous current inputs and electrical
impedance resistance sensors in different locations around the flow boundary (along with a complicated computer algorithm), a characterization of flow and compositions within the domain can be created\textsuperscript{70,71}. Pertinent data such as void fractions, spatial distributions, and flow characteristics can then be evaluated utilizing this technique\textsuperscript{72}.

Electrochemical methods have previously been used to determine the liquid-solid wetting area on the surface throughout the boiling regimes\textsuperscript{73-77}. Dhuga\textsuperscript{75,76} and Rajabi\textsuperscript{77}, in particular, monitored changes in current through a substrate coated with a dielectric insulating layer during the process of pool boiling in nucleate, transition, and film boiling. This dielectric layer, however small, plays some role in the surface conditions. A technique that did not incorporate direct surface contact with a dielectric insulating layer can provide valuable fundamental information of boiling mechanisms and liquid-solid interfacial properties without changing surface conditions.

1.4. Summary

Thermal management is, and will continue to be, a major concern in design of new electronic systems. Current limitations in cooling technologies are leading to overheating of system components and failure of critical system operations. Pool boiling studies are necessary in evaluating new cooling techniques using liquid to vapor phase change systems. These studies provide means of characterizing both multiphase fluids and engineered surfaces. Active control of two-phase cooling technologies could provide a means to simplify engineering designs and allow for a more efficient scheme. A method that provides control over liquid to vapor phase change processes is altering the surface energy by exposure to UV light. Photonic excitement of surfaces can chemically and physically alter the surface in a way that increases or decreases affinity to
the boiling fluid. Photoactive surfaces such as copper, TiO$_2$, and carbon nanotubes have been studied under light irradiation and have been shown to exhibit a chemical change under light exposure. Mechanisms for the conversion of surface energies have not been fully investigated in a pool boiling environment.

A method for potentially measuring in-situ surface energy during boiling experiments is through Electrochemical Impedance Spectroscopy (EIS). By isolating the vastly different electrical conductivities of both water and air, fundamental boiling information can be determined during the boiling process.
CHAPTER II
RESEARCH OBJECTIVES

The objectives of the research are as follows:

1. To investigate changes in critical boiling parameters such as HTC and CHF upon light irradiation of copper, titanium dioxide thin films, and multiwall carbon nanotube arrays.

2. To correlate mechanisms to the chemical and physical surface changes of copper, titanium dioxide thin films, and CNT arrays due to the coupled effect of liquid to vapor phase change processes and UV light exposure.


To accomplish the first two objectives, photoactive substrates were manufactured, pool boiling experimentation was performed, and surface analysis techniques were incorporated to mechanistically study three known photoactive materials. The third research objective led to the incorporation of electrochemical techniques on pool boiling studies of copper and could be extremely useful in studying fundamental boiling processes.
CHAPTER III

EXPERIMENTAL METHODOLOGY

3.1. Substrate Preparation

The base substrates used for the pool boiling experiments were CDA 110 99.6% commercially pure copper that were 2.54 cm diameter and 0.22 cm thick. Two different subsets of samples were created with varying roughness. In the first set of samples, bare copper substrates were roughened with 400 grit sandpaper in a “figure 8” pattern to ensure random scratches throughout the surface. This technique yielded micron-sized scratches on the surface with RMS roughness features, measured by a profilometer, at 520 ± 36 nm. The second set of samples, ones that required some sort of deposition or growth, were polished to an extremely fine mirror finish in a series of four steps. First, the 0.22 cm thick copper samples were polished exactly the same way as the roughened substrates with 400 grit sandpaper on a polishing wheel. Then, the wheel was coated with 800 grit silicon carbide sandpaper and polished to uniform roughness. The third step required a lapping procedure using a Gold Label polishing cloth and a 9 µm polycrystalline diamond paste. Finally, all of the visible scratches on the substrate are polished off with a Microcloth polishing cloth and 1 µm polycrystalline diamond paste. Characterized by a profilometer, the RMS roughness on these polished samples was 14 nm ± 2.0 nm. Uniformity in boiling experiments and deposition is imperative and using this technique yields repeatable roughness features. Also, because typical bubble
formations and departure sizes are on the order of tens of microns, the roughness features are well below critical length scales for these types of heat transfer experiments.

### 3.1.1. Titanium Dioxide Deposition

Magnetron sputtering is a physical vapor deposition (PVD) technique that can deposit thin films of various metals, metal oxides, semiconductors, and various other types of materials. Titanium dioxide thin films were deposited on the polished copper substrates by a specific type of magnetron sputtering known as reactive sputtering. Reactive sputtering involves a chemical reaction between the target material and a gas introduced in the chamber and has been used to deposit thin films of metal oxides on substrates.

The substrate was cleaned via sonic bath for 30 minutes in acetone to remove common contaminants prior to being loaded into a deep vacuum deposition chamber. Once in the chamber, the substrate was further cleaned using an argon etching technique by flowing argon into the chamber at 50 sccm and controlling the pressure at 5.33 Pa. An 800 V bias was then slowly applied to the substrate holder and left on for 2 hours. The argon etching process is extremely important in the deposition of copper in order to remove surface layers of copper oxide, caused by exposure to air in sample transportation. By removing this monolayer coverage of copper oxide, a controlled surface condition of pure metallic copper allows for better film adhesion. After the argon etching process, the sample bias was reduced to 50 V and the system pressure was reduced to 2.0 Pa. The sample stage was then continually slowly rotated to allow for a uniform sputtered coating. A pulsed DC power supply operated at 80 kHz and 70 W with a 0.4 μs delay time between pulses was used for magnetron sputtering of a 3.30 cm
diameter titanium dioxide target. First, pure titanium was sputtered for 20 minutes on copper substrate to act as an intermediate adhesion layer. Then, oxygen flow to the chamber was initiated at 25 sccm for 70 minutes while maintaining Ar flow at 50 sccm. The oxygen in the chamber will react with the titanium and create the thermodynamically stable form of titanium dioxide. Film thickness can be controlled by the length of deposition times and varying deposition rates. From previous deposition experiments, the film thickness is estimated to be around 300-500 nm.

3.1.2. Carbon Nanotube Deposition

Carbon nanotube deposition procedures used to form films of CNTs have been investigated intently due to advantageous thermal and mechanical properties from the arrays. In this study, multi-walled CNT films were deposited by means of microwave plasma chemical vapor deposition (MPCVD) at Purdue University by Arun Kousalya. The growth procedure began with the deposition of a trilayer catalyst of 30 nm of titanium, then 10 nm of aluminum, followed by 3 nm of iron on the copper substrates. Hydrogen gas at 50 sccm and methane at 10 sccm were introduced into the vacuum deposition chamber, while the growth pressure and temperature were maintained at 1.33 kPa and 900°C. CNT synthesis was allowed to continue for 10 minutes. The deposition yielded a dense and randomly oriented array of nanotubes on the surface, with the diameter of the tubes ranging from 30-80 nm. A detailed analysis of the films and characterization to confirm existence of nanotubes via Raman is given in previous studies using the same deposition method as in this study.\textsuperscript{43,81,82}
3.2. Pool Boiling Experiments

3.2.1. Apparatus

The pool boiling apparatus featured a test chamber that encompassed the phase change liquid along with the steel protective base plate in which the experimental substrates were placed during boiling experiments. Test chamber walls consisted of double paned quartz glass to ensure minimal heat loss from the pool of stagnant water and to allow viewing the solid-liquid-vapor interface through the glass. The chamber was coated in aluminum foil during boiling experiments both under UV-irradiation and non-irradiation to reflect some scattered lamp output light back inside the chamber and to the substrate.

The chamber was filled with approximately 700 mL of 18.2 MΩ-cm ultrapure deionized ASTM/CAP/NCCLS Type I water. To maintain the water at just below the saturation temperature, required for saturated boiling experiments, a Digisense Temperature Controller Model R/S connected to two thermocouples located within the liquid monitored pool temperature. The Digisense system interpreted the temperature and controlled the operation of two stainless steel firerod heaters (0.32 cm OD, 8.89 cm length) located at the base of the test cell and assisted in heating at subcooled temperatures.

The test substrates were anchored at the base of the pool boiling test cell by a Teflon gasket and secured by a stainless steel plate. One 0.064 cm hole drilled 1.27 cm in the side of the substrate allowed for insertion of a 40 gauge Omega T-type thermocouple to monitor copper surface temperature. A cylindrical firerod heater (1.26 cm diameter, 7.62 cm length) located directly beneath the substrate provided heat flow to
the samples and was controlled by an Agilent 3060A 1000W power supply. A larger cylindrical copper block encompassed the heater and three T-type thermocouples provided a means to calculate one dimensional heat flux from the heater to the substrate. This block was surrounded by a thin layer of very low thermal conductivity MICROSL microporous insulation to minimize heat losses in the non-axial direction. An insulation thickness of 0.95 cm provided a significant thermal barrier and provided for a total heat loss in the non-axial direction of only around 5%. A small amount of Omegatherm 201 thermal grease (k=0.019 W/m·K at 20°C) was placed on the top surface of the copper block and the bottom surface of the substrate in order to provide a conductive interface from the heater block to the backside of the samples of interest.

Two experimental configurations for sample holders were used in the pool boiling experiments and are illustrated in Figure 17. Configuration #1, used in the copper boiling experiments, consisted of a Teflon gasket machined to anchor the substrate in place as well as to provide a shield from lateral liquid flow below the substrate and to the copper block. A significant amount of waterproof Silicone RTV sealant was used underneath the Teflon gasket to ensure an air gap was maintained between the heater block and the liquid pool. If this sealant was not in place, liquid would contact the outsides of the heater block and increase the surface area for boiling on the sides of the block. The thermocouple was threaded through the side of this sealant when it was first applied and exited through the steel plate at the top of the apparatus. Although this provided an efficient seal with minimal leakage, boiling tests could not be performed immediately because the silicone had to cure for at least 24 hours before use. In Configuration #2, used in the titanium dioxide and carbon nanotubes testing, the Teflon piece was re-
engineered with a side “skirt” along with a groove cut in the base to accompany a Viton o-ring. A small hole was cut in the o-ring to thread the surface thermocouple through, and once the o-ring was compressed a seal would be made between the o-ring and thermocouple. Both of the configurations ensured a unidirectional heat transfer rate to the surface, but Configuration #2 yielded a much lower chance of contamination along with a quicker turnover time because there was no requirement to wait before a boiling run could be started. A stainless steel cover was placed over the Teflon piece with three screws and springs to apply compression force on the substrate. This helps decrease the thermal resistance from the Omegatherm 201 thermal grease and the springs are important to allow thermal expansion from the copper sample when the temperature is increased.

![Figure 17: Illustrations of sample a) Configuration #1; and b) Configuration #2](image)

A stainless steel top plate is placed on top of the quartz cylinder. The two pool thermocouples extend from this top plate into the liquid pool approximately 2 inches
from the sample to measure pool temperature. A one and one half inch opening in the middle of the plate allows for the collimated UV-visible light to pass through and into the chamber.

3.2.2. Heat Flux Calculations

The copper block used to house the thermocouples is depicted in Figure 18. Heat flux was measured by using thermocouples TC1, TC2, and TC3 embedded within the copper block. Fourier’s law of heat conduction is then used to determine a heat flux value by taking the average of the heat flux between each of the thermocouple sets. The block itself has a significant diameter change towards the top in order to accommodate for 1” OD samples. In order to distinguish between the change in area, $q_H$ is designated as being the heat flux at the larger diameter of the copper block, and $q_S$ is the smaller diameter at the top of the block. The measured temperatures, thermal conductivity of copper and the distance between the thermocouples ($x_1$ and $x_2$) generates the heat flux at the heater dimensions from the equation

$$ q_H = \frac{-k_{avg\ 3.2} \frac{T_2 - T_3}{x_2} - k_{avg\ 2.1} \frac{T_1 - T_2}{x_1} - k_{avg\ 3.1} \frac{T_1 - T_3}{x_1 + x_2}}{3} $$  \hspace{1cm} (10)

The heat flux reported in the boiling experiments, $q_S$ is then formulated by taking the ratio of the area of the base of the block, $A_H$, to the boiling surface area, $A_S$,

$$ q_S = q_H \frac{A_H}{A_S} $$  \hspace{1cm} (11)
Figure 18: Illustration of copper block with heat flux thermocouples

The thermocouples used for the heat flux measurements were 32 gauge T-type thermocouples constructed with Special Limits of Error materials and rated to an accuracy of within 0.5°C. The thermocouple calibration procedure was performed by encompassing the entire block in a completely insulating carbon fiber material. The heater located at the base of the block is turned on at various powers and the thermocouples were allowed to equilibrate. Once the temperatures equilibrate after an extended period of time, temperature measurements were taken until the thermocouples were calibrated up to 300°C. Temperature data from the calibration can be seen in Table 2. The temperature data presented is well within error of the thermocouples themselves.
and it was determined that the thermocouples did not need to be further calibrated beyond factory standard limits of error.

Table 2:  Heat flux thermocouple calibration run

<table>
<thead>
<tr>
<th>Heater Power (W)</th>
<th>TC1 (°C)</th>
<th>TC2 (°C)</th>
<th>TC3 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25.11</td>
<td>25.14</td>
<td>25.14</td>
</tr>
<tr>
<td>5.6</td>
<td>51.70</td>
<td>51.70</td>
<td>51.74</td>
</tr>
<tr>
<td>10.5</td>
<td>75.89</td>
<td>75.93</td>
<td>75.93</td>
</tr>
<tr>
<td>14.5</td>
<td>110.40</td>
<td>110.41</td>
<td>110.47</td>
</tr>
<tr>
<td>19.8</td>
<td>136.03</td>
<td>136.05</td>
<td>136.10</td>
</tr>
<tr>
<td>25.1</td>
<td>170.88</td>
<td>170.92</td>
<td>170.99</td>
</tr>
<tr>
<td>30.4</td>
<td>196.24</td>
<td>196.26</td>
<td>196.33</td>
</tr>
<tr>
<td>35.9</td>
<td>250.21</td>
<td>250.27</td>
<td>250.33</td>
</tr>
<tr>
<td>42.5</td>
<td>277.33</td>
<td>277.36</td>
<td>277.46</td>
</tr>
<tr>
<td>48.2</td>
<td>316.63</td>
<td>316.65</td>
<td>316.76</td>
</tr>
</tbody>
</table>

The surface thermocouple used in the boiling experiments was calibrated to the same specifications as those used in the heat flux calculations. The 40 gauge thermocouples were constructed of materials that were held to the standards of Special Limits of Error and were replaced frequently to ensure that the integrity of the thermocouple was intact.

3.2.3. Pool Boiling Experiments

Pool boiling experiments were aided with the use of a Labview program that displayed results and provided the ability to control the main and pool heaters. The heat flux calculations, pool boiling curves, and temperature plots enabled real time analysis of data to detect steady state conditions and any potential issues that could arise.
Once the apparatus setup was complete and filled with water, the pool was slowly brought up to a temperature of 50°C by using the pool heaters. After this point, the setpoint of the PID controller for the pool temperature was set to 99°C and the main heater was turned on to a power of 100 W. The pool temperature was allowed to increase to the saturation temperature and then the main heater was kept on for a period of thirty minutes. At this point, vapor bubbles form and depart from the surface under partially developed nucleate boiling conditions. This procedure is necessary to remove dissolved oxygen and nitrogen gas from the water and effectively works as an “aging” procedure to equilibrate the surface conditions. After the thirty minutes of boiling and the dissolved gases are driven off, the main heater is turned off and the surface is allowed to reach a temperature of 100°C. Then, the Labview program begins to accumulate data as the heater power is increased to 30 W. Once the temperature has reached equilibrium after approximately 8 minutes, the average three measurements of the temperature and heat flux are recorded in a notebook and the heater power is increased by 30 W. This trend is carried on throughout the boiling experiment until either the desired heat flux is reached or CHF occurs. Once all of the data points are collected, the main and pool heaters are turned off and the system is allowed to return to room temperature. The sample is then removed and placed in a desiccator to prevent oxidation before further surface analysis.

### 3.2.3.1. Critical Heat Flux Value

The CHF point in the boiling experiments is very easily recognized by a sudden and rapid increase in temperature and significant decrease in heat flux. The heat flux values prior to this point that make up the boiling curve are taken at steady state, but the CHF value is a transient condition. The Labview program records the heat flux and surface
temperature values throughout the experiment at approximately one data point per second. The CHF value is recorded as the average of the five data points prior to the rapid increase in temperature. This provides an accurate estimation of the CHF value during transient boiling changes.

3.2.3.2. Heat Transfer Coefficient

The heat transfer coefficient (HTC) during the nucleate boiling regime is an important parameter in determining boiling heat dissipation rates. A higher HTC would indicate a better removal of heat via phase change than a lower HTC. The HTC in the boiling tests is determined by taking the slope of the steady state heat flux and surface temperature values of the nucleate boiling curve starting at 40 W/cm$^2$. This heat flux was chosen as the baseline to the initiation of fully developed nucleate boiling.

3.2.4. Light Irradiation

The 1000W Xenon-Mercury arc lamp produces a broadband high powered UV-visible light. An output spectrum is shown in Figure 19. For the copper boiling experiments, the lamp was mounted at a 30 degree angle from the substrate and then passed through a small window that was not covered by the aluminum foil. For the titanium dioxide and carbon nanotube experiments, the light was mounted above the boiling apparatus. A lens placed directly below the light source collimates the beam of light below the one and a half inch hole in the top plate and then the diameter expands to cover the substrate in the chamber.
The lamp input power was set to 800 W for the copper experiments and then
down to 500 W for the titanium dioxide and CNT experiments. The reason this was done
was to extend the life of the bulb in the lamp due to the long irradiation times required for
the titanium dioxide and CNT tests. Irradiation power was measured using a Coherent
model LM-1 HTD sensor at different input power ratings. Figure 20 displays the output
power as a function of the input power setting.

Figure 20: Light intensity of broadband light source with different power inputs
Tests were also performed to determine the effect of light scattering through water at the same depth that the samples are placed during boiling tests. Additionally, a nitrogen gas line was placed in the water to simulate bubble formation and to give insight into how much light actually reaches a surface during boiling. The resulting light energy fluxes are shown in Table 3. A significant loss in light energy is present through the liquid pool and an even larger loss with the addition of gas bubbles.

Table 3: Light irradiation measurements in mW/cm²

<table>
<thead>
<tr>
<th>Description</th>
<th>500 W</th>
<th>800 W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light through quartz beaker</td>
<td>273</td>
<td>436</td>
</tr>
<tr>
<td>Light through quartz beaker encompassing 700 mL of water</td>
<td>154</td>
<td>247</td>
</tr>
<tr>
<td>Light through quartz beaker encompassing 700 mL of water, nitrogen bubbles</td>
<td>70</td>
<td>112</td>
</tr>
</tbody>
</table>

It is important to note that the light energy flux is at the very least two orders of magnitude less than the heat flux coming from the main heater. Therefore, the heat stemming from the broadband light source is thought to not have an influence on the boiling surface temperature.

3.2.5. Electrochemistry Setup

Electrochemical monitoring was achieved with a Gamry EIS 300 Electrochemical Impedance Spectroscopy System, allowing for in-situ measurement of both impedance and open circuit potential during boiling. The copper substrate working electrode was complemented electrically with a platinum mesh counter electrode and a Ag/AgCl
reference electrode, both submerged in the pool in a non-intrusive manner to complete the electrochemical circuit.

The 18.2 MΩ·cm ultrapure water could not be used as the boiling fluid because it is designed to be nonconductive, and thus provided a significant contribution to the overall impedance measurements. To combat this resistance, a small amount of NaCl was added to the ultrapure water to increase the conductivity. An initial concentration of 5 mMol was determined experimentally to be the minimum concentration of salt required to provide effective electrical conductivity.

Electrochemical impedance measurements were taken throughout the boiling experiment in the nucleate boiling regime and through the transition point from nucleate to unstable film boiling at a frequency of 1000 Hz. A single frequency monitoring of impedance during boiling is performed in this study to provide a better understanding of transient physical characteristics in a boiling situation. A frequency sweep of impedance data collection could potentially be done at steady-state points in future experiments. An open circuit potential was recorded prior to the impedance spectrum and a slight cathodic polarization of -100 mV DC versus the measured open circuit potential was applied to the working electrode with 10 mV AC amplitude. For impedance measurements, an average of 10 impedance points at steady state were averaged and the standard deviation reported as error bars.

Once the point from nucleate to transition, or unstable, film boiling was reached and a thin unstable vapor film was observed, the heater power remained constant in order to monitor transient properties of the solid-liquid-vapor system. At the point of minimum
heat flux and entrance into the fully developed film boiling regime, the heater was turned off to ensure that the system was not damaged from extremely high temperatures.

### 3.3. Surface Analysis

Surface analysis was performed before and after nucleate boiling experiments to determine critical information regarding surface structuring, chemical composition, and crystal structure.

#### 3.3.1. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) imaging was imperative to boiling studies in order to characterize surface features of different sizes and morphology, and to characterize the change of the surface due to boiling and light exposure. This analysis was performed using a Quanta II microscope that could provide high resolution imaging.

#### 3.3.2. X-Ray Photoelectron Spectroscopy

X-Ray Photoelectron Spectroscopy (XPS) analysis was performed with a SSI and Kratos Ultra DLD spectrometer using monochromatic Al Ka radiation (1486.6 eV) operated at $1.3 \cdot 10^{-7}$ Pa ($1 \cdot 10^{-9}$ Torr) base pressure. The main difference between the two XPS instruments is that the SSI tends to have a slightly higher amount of background noise. Most of the analysis, therefore, was performed on the Kratos Ultra DLD spectrometer. Prior to the analysis, sample surfaces were cleaned from atmospheric adsorbents using a 45 second exposure to a 5 kV low current Ar ion beam directed at a 60 degree angle to the sample surface. The survey and high energy resolution spectra were collected from a 700x400 µm² spot, with the X-rays irradiating the surface at normal incidence using fixed analyzer pass energies of 160 and 20 eV, respectively. The
obtained spectra were analyzed with commercially available CasaXPS software with individual peaks fitted with a Gaussian-Lorentzian function and a Shirley background subtraction. Spectrometer sensitivity factors and photoelectron escape depth variation for the analyzed elements were taken into account with the software analysis. The XPS analysis typically only penetrates several nanometers into the film itself, and so this technique was very advantageous for boiling heat transfer surfaces that are mainly concerned with monolayer surface composition.

3.4. Contact Angle

In order to quantify surface energy, contact angle measurements were performed using a Attension Theta Optical Tensiometer equipped with OneAttension analyzing software that analyzes an image of a droplet and reports the angle of incidence between the liquid and solid. The liquid dispenser gently places a 1 µL droplet of ultrapure water on the substrate, and then optically measures the contact angle by means of a programmed Young’s equation curvature estimation. The droplet is allowed to equilibrate and an average of the left and right contact angle results is taken after 10 seconds. Three different spots on the surface were measured and averaged to achieve an overall surface energy estimation.

It is important to note that the contact angle goniometer was not equipped with a Peltier stage that would allow for temperature control of the surface. Contact angle experiments were performed at room temperature and the assumption is made that the contact angle does not significantly change with increasing temperature. Future experiments investigating contact angle changes with temperature would aid this study.
CHAPTER IV
RESULTS AND DISCUSSION

4.1. Photoboiling Results

Pool boiling tests were performed on copper, titanium dioxide, and carbon nanotube substrates to experimentally determine the effects of UV-visible light on boiling behavior of these surfaces. In conjunction with this study, small scale contact angle measurements were performed and mathematical models were utilized to test predicted values with actual values of boiling results.

4.1.1. Copper

Pool boiling experiments on roughened copper substrates prepared as described in Section 3.1 can be seen in Figure 21. The boiling test without light was initially performed and was allowed to reach the CHF condition. Runs 1-3 were performed using the same procedure up to a heat flux of 60 W/cm², and then the Xe(Hg) lamp was turned on at a power of 800 W. After a period of time, the CHF condition was reached in Runs 1 and 2, but was not reached in Run 3 after 1 hour of nucleate boiling. The observation, however, was that the liquid-vapor interface in this run entered a meta-stable state in which the morphology switched back and forth between nucleate and film boiling. The film boiling mode typically lasted for less than a second before reverting back to nucleate boiling mode. This morphology switch was noted in Runs 1 and 2 before the CHF
condition. Variation of the copper samples is thought to be due to differences in sample preparation and experimental variations.

![Graph: Pool boiling curves for roughened copper substrates](image)

**Figure 21: Pool boiling curves for roughened copper substrates**

Surface temperature measurements were taken before and after the UV-visible light source was turned on and can be seen in Figure 22. The surface temperature in all three experiments dropped by 0.5-1.0°C within several minutes of the light exposure. Further characterization was necessary to determine the mechanism behind the drop in surface temperature.
Scanning Electron Microscopy (SEM) characterization was performed on the samples to determine any morphological changes that occurred during the boiling process and when exposed to light. The irradiation setup for the copper boiling experiments was done at a 45° angle. This caused the edge of the substrate to be shielded from the lamp due to the Teflon gasket sample holder. SEM images of this shielded region, shown in Figure 23a, of the substrate tested to CHF during light irradiation compare very closely to an as-prepared copper sample and can be seen in Figure 23b. The morphology of the irradiated and boiled on to CHF sample is seen in Figure 23c with the presence of nano-sized features and micro-sized clusters of these features. A close-up view of these clusters can be seen in Figure 24. These clusters were observed in multiple runs but only in the boiled on irradiated sample. Imaging of an irradiated sample in laboratory air only, seen in Figure 23d, does not exhibit these nanostructures and resembles the control surface.
morphology. Therefore, these surface morphologies appear to be a result of a combination of light exposure and boiling and not by either condition individually.

Figure 23: SEM micrographs of roughened copper substrates: a) shielded region of substrate from Xe(Hg) light source during boiling; b) unexposed surface (no boiling or light exposure); c) center of the sample after pool boiling testing to CHF during exposure to light source; d) after 18 hours of light exposure in lab air
In addition to SEM, the four copper substrates were characterized using X-ray Photoelectron Spectroscopy (XPS). The analysis determined that the samples contained copper, oxygen, and trace amounts of carbon and chlorine impurities. These impurities were associated with sample handling and exposure to air. Survey spectra indicate that the dominant species present were copper and oxygen. High energy resolution scans were then performed for the Cu 2p and O 1s regions to allow detailed investigation of the chemical state of the samples. The binding energy of the Cu 2p\textsubscript{3/2} XPS peaks for all four surfaces was 932.7 eV, which indicates the presence of either metallic copper or Cu\textsubscript{2}O\textsuperscript{83-}\textsuperscript{85}. There was no strong presence of CuO for which the Cu 2p\textsubscript{3/2} peak occurs at 933.8 eV. The degree of the oxidation was more clearly seen from comparison of oxygen O 1s peaks in Figure 25, which shows high energy resolution XPS scans from the four
samples. The most oxidized was the sample after UV exposure in air, followed by the sample with UV light exposure during boiling, and then by the sample after boiling with no UV light. A copper control sample that exhibited no boiling or UV exposure is also included in Figure 25. All O 1s peaks exhibited a higher bonding energy shoulder, which was associated with hydroxyl group attachments. Peak fitting was performed to distinguish between oxygen bonded in hydroxyl groups (O 1s at 532.3 eV) and oxygen in Cu$_2$O (O 1s at 530.5 eV). An example of copper oxide and hydroxyl component fitting is shown in the inset of Figure 25. The largest hydroxyl component was present for the sample after boiling without UV before CHF, indicating a possibility of higher percentage Cu(OH)$_2$ formation compared to the other samples. The surface of all samples was found to contain mostly Cu$_2$O oxides. The degree of the oxidation was varied, with the strongest oxidation observed for the samples exposed to UV light. Also, UV exposure during boiling provided a less oxidized surface state compared to UV in air. Cu$_2$O is a well known UV absorption material with reported photocatalytic activity under exposure to UV light$^{86,87}$, which may lead to water splitting, formation of hydroxyl groups and further copper oxidation. It is therefore likely that the oxide formation on the copper surface is both accelerated by UV light exposure and is critical for coupling UV energy to the surface.
The proposed mechanisms of copper oxide and hydroxyl formation can be traced back to elementary chemical reactions. Nucleate boiling on copper without light exposure and under the conditions of heat and boiling yields formation for Cu(OH)$_2$ from the reaction

$$ Cu + 2H_2O \xrightarrow{\text{Heat, boiling}} Cu(OH)_2 + H_2 $$

(12)

The light irradiation sample exhibits decomposition of the Cu(OH)$_2$ compound under UV light to a more stable Cu$_2$O under the following reaction
The copper exposure to light in air, however, does not incite the formation of \( \text{Cu(OH)}_2 \) due to the lack of water present to form the copper hydroxide. Instead, the formation of copper oxide in air follows the reaction mechanism

\[
4\text{Cu} + \text{O}_2 \xrightarrow{hv} 2\text{Cu}_2\text{O}
\]  

The reactions for copper oxide formation are not the only driving reactions in the process, but appear to be the dominant in each individual case, determined by XPS analysis. More experimentation is necessary to completely define the mechanisms proposed.

The reaction that includes the formation of copper oxide nanocrystals and decomposition of the copper hydroxide could be the mechanism driving the temperature decrease after light exposure seen in the boiling experiments. This hypothesis is due to the fact that the enthalpy of reaction calculations, based on the enthalpy of formations, indicates an endothermic reaction because of the positive heat of reaction of 1461 kJ/mol.

The calculation of the heat of reaction is seen below:

\[
\Delta H^0_{\text{rxn}} = \sum v_p \Delta H^0_f(\text{products}) - \sum v_r \Delta H^0_f(\text{reactions})
\]

\[
\Delta H^0_{\text{rxn}} = \left[ v_{\text{Cu}_2\text{O}} \times \Delta H^0_f(\text{Cu}_2\text{O}) + v_{\text{O}_2} \times \Delta H^0_f(\text{O}_2) + v_{\text{H}_2} \times \Delta H^0_f(\text{H}_2) \right] - \left[ v_{\text{Cu(OH)}_2} \times \Delta H^0_f(\text{Cu(OH)}_2) \right]
\]

\[
\Delta H^0_{\text{rxn}} = \left[ 2 \times (-166.5 \frac{\text{kJ}}{\text{mol}}) + 3 \times (0 \frac{\text{kJ}}{\text{mol}}) + 4 \times (0 \frac{\text{kJ}}{\text{mol}}) \right] - \left[ 4 \times (-448.5 \frac{\text{kJ}}{\text{mol}}) \right]
\]

\[
\Delta H^0_{\text{rxn}} = 1461 \frac{\text{kJ}}{\text{mol}}
\]

The energy associated with the formation of the copper oxide nanoclusters draws thermal energy away from the surface causing a drop in surface temperature. Verification of this
hypothesis would require a gas trap to collect stoichiometric ratios of hydrogen and oxygen, and was not included in this work.

Contact angle tests were also performed on the surface to monitor changes in surface energy when exposed to UV light energy. Optical images were captured using a contact angle goniometer in laboratory air and exposure to an input value of 800 W lamp power for 18 hours. The data can be seen in Figure 26 and images can be seen in Figure 27. Both pre- and post-boiling copper substrates exhibited an increased contact angle with increased UV exposure. The wettability change observed in these experiments was a result of the surface oxidation from the UV-VIS irradiation. Since the oxidation also occurred during nucleate boiling, the induced CHF at lower than expected heat flux values under the light exposure correlates with the increase in contact angle.

![Graph showing contact angle changes during lamp exposure in laboratory air](image)

**Figure 26:** Contact angle changes during lamp exposure in laboratory air
Boiling results, contact angle testing, XPS, and SEM confirm that a combination of chemical oxidation as well as a morphological surface change contributes to the photoactivity of copper in pool boiling tests. Results indicate a variance in the boiling data that is attributed to the roughness of the sample and a complex changes in surface chemistry.

4.1.2. Titanium Dioxide

Titanium dioxide samples were made using reactive sputtering techniques discussed in previous Section 3.4.1. XPS and SEM analysis were performed post deposition and determined that the film was stable but yielded small amounts of contaminants of gold and zinc, likely contaminated from the deposition chamber in which magnetron sputtering and other material synthesis is performed. SEM image and XPS spectra of as-deposited titanium dioxide are shown in Figure 28. The SEM image depicts a relatively smooth film with very few defects, even at relatively high magnifications.
XPS data show a very clean, stoichiometric ratio of peaks from both titanium and oxygen. A small peak from copper and a small carbon impurity appear potentially due to small pits in the film and physioabsorbed carbon dioxide, respectively.

Figure 28: a) SEM Image and b) XPS spectra of as-deposited TiO$_2$ sample

 normalized intensity
Titanium dioxide pool boiling tests were performed in multiple sets of experiments. Set 1 involved testing to determine changes in ONB temperature along with changes in HTC upon UV-VIS exposure. In parallel to the boiling experiments, contact angle experiments were performed on a separate sample (Sample #2) subjected to the same time of water immersion and light exposure for comparison purposes. The TiO$_2$ sample used in boiling tests (Sample #1) was never removed from the apparatus during the experiments. Set 2 testing was to determine changes in CHF due to light exposure. Two separate samples were used for these tests (Sample #3 and Sample #4) due to the destructive nature of the boiling process beyond CHF conditions. An outline of the experimental tests is seen in Table 4.

<table>
<thead>
<tr>
<th>TiO2 Samples</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Extended long-term boiling tests under water immersion and UV irradiation</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Contact angle experiments performed on sample subjected to same water immersion and UV irradiation times as Sample 1, but without boiling</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Boiling test to CHF without light</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Boiling test to CHF with light irradiation for 53 hours</td>
</tr>
</tbody>
</table>

Set 1 experimentation began with three boiling curves without UV-VIS light exposure to determine initial ONB temperatures and HTC and the subsequent changes due to immersion in ultrapure water. Then, the light source was turned on and numerous tests followed with varying degrees of irradiation time, as outlined in Table 5. The fully developed nucleate boiling curve from a heat flux of 40 W/cm$^2$ to 60 W/cm$^2$ is shown in Figure 29 and the complete boiling curve can be seen in Appendix B. The heat transfer
coefficient of each boiling run, found from the method discussed in Section 3.2.3.2, can be seen in Figure 30.

Table 5: Description of testing procedure for TiO$_2$ Sample 1

<table>
<thead>
<tr>
<th>Run #</th>
<th>Description of Titanium Dioxide Testing Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>Sample placed in apparatus in darkness with water, left 24 hours then began boiling run</td>
</tr>
<tr>
<td>Run 2</td>
<td>Water drained immediately after Run 1, refilled, and sample kept in apparatus in the dark after Run 1, and boiling run began 24 hours later</td>
</tr>
<tr>
<td>Run 3</td>
<td>Water drained immediately after Run 2, refilled, and sample kept in apparatus in the dark after Run 1, and boiling run began 4 hours later</td>
</tr>
<tr>
<td>Run 4</td>
<td>Water drained immediately after Run 3, refilled, and lamp turned on at 500W, boiling run began 24 hours later</td>
</tr>
<tr>
<td>Run 5</td>
<td>Water drained immediately after Run 4, refilled, and lamp kept on at 500W, boiling run began 4 hours later (29 hours of light irradiation)</td>
</tr>
<tr>
<td>Run 6</td>
<td>Water drained immediately after Run 5, refilled, and lamp kept on at 500W, boiling run began 19 hours later (48 hours of light irradiation)</td>
</tr>
<tr>
<td>Run 7</td>
<td>Water drained immediately after Run 6, refilled, and lamp kept on at 500W, boiling run began 4 hours later (53 hours of light irradiation)</td>
</tr>
<tr>
<td>Run 8</td>
<td>Water drained immediately after Run 7, refilled, lamp turned off and sample kept in darkness for 120 hours, then boiling run began</td>
</tr>
</tbody>
</table>
Figure 29: Nucleate pool boiling data for TiO$_2$ Sample 1 and corresponding HTC values

Figure 30: HTC change from titanium dioxide boiling experiments under light exposure
Run 1, 2, and 3 experienced minimal differences in both ONB condition and nucleate boiling heat transfer coefficient. In the absence of light irradiation, the surface has a significant decrease in the amount of electron-hole pairs required for the hydroxyl group affinity and eventual hydrophilic conversion. Also, the violent boiling mechanism appears to have little effect on the surface characteristics in the region of testing, as evident in the lack of a physical change to the critical boiling parameters. Parallel contact angle testing, as seen in Figure 31, indicates a slight change in contact angle upon water immersion towards a more hydrophilic surface energy. The change in hydrophilicity in small scale controlled contact angle testing, however, did not appear to have a significant effect on the boiling performance in the absence of light energy.

Figure 31: Contact angle results on Sample #2
Once the lamp is turned on, a significant change in both boiling performance and contact angle is observed. The boiling results of fifty three hours of irradiation indicate a shift in both the ONB temperature and HTC. Due to the change in surface energy, a drop in HTC is evident upon longer exposure to light irradiation. Over a period of 53 hours, a 16.8% drop in HTC in the boiling experiment and a 55.3% drop in contact angle is observed. Both of these trends agree well with what would be expected from a smooth surface. The ONB temperature, however, seems to decrease with increasing hydrophilicity, which appears to be counter-intuitive to typical boiling results. SEM imaging tests show little change in the overall morphology of the surface. XPS results taken after the conclusion of the boiling tests on Sample 1, however, indicate a change in surface characteristics, which could explain the decrease in initial boiling temperature. XPS comparison before and after boiling on Sample 1 can be seen in Figure 32. An increase in copper concentration on the surface indicates some sort of contamination during the boiling process. Correlating to the boiling tests, it appears to have initiated after the exposure to UV-light, where a shift in the ONB point is evident. A sputtering XPS technique was used to sputter through the sample and determine the concentration profile through the film. Once the initial copper layer was penetrated, pure titanium dioxide was seen in the underlayers indicating a small surface concentration of copper contamination. Future tests are needed to determine whether this was a product of light exposure increasing the affinity for copper deposition, or if this was a source of contamination due to sample preparation techniques.
Set 2 of boiling tests were performed on two separate samples to determine UV irradiation effects on pool boiling CHF. Each sample was immersed in water for a total of 77 hours, where Sample 3 was covered with aluminum foil and left in complete darkness, and Sample 4 was irradiated with light for the last 53 hours. The final CHF tests began at the 77 hour mark for each and results are seen in Figure 33. A significant variation in the overall HTC is evident, which a slight delay of the onset of nucleate boiling point. This result is to be expected for increasingly hydrophilic conversion. The CHF condition was delayed slightly in the case of light exposure, but is not considered to be of significant variance and outside the realm of error for the CHF.
Zuber and Kandlikar’s CHF prediction method was used to compare to the boiling results from the titanium dioxide tests in Table 6. Kandlikar’s model predicts an increase in CHF value with a decrease in surface energy, which correlates well to both the contact angle and boiling results. Due to the superhydrophilicity of the titanium dioxide both before and after light exposure, the change in CHF condition is not so drastic as to provide a significant difference in CHF values. The model used by Kandlikar also over-predicts the CHF condition by a substantial amount. One hypothesis to this occurrence is that the model used in his predictions is for an infinite plate with no edge effects. In the apparatus used in the boiling tests, the Teflon ridge of the sample holder has some impact on the sample system and could potentially decrease CHF by limiting the amount of
liquid replenishment area. Zuber’s CHF prediction actually comes very close to the appropriate value, although it does not account for surface energy or surface properties as a dominating mechanism.

Table 6: CHF values for titanium dioxide boiling tests and models

<table>
<thead>
<tr>
<th>Description</th>
<th>CHF Value (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ without light, measured experimentally</td>
<td>98.4</td>
</tr>
<tr>
<td>TiO₂ with light, measured experimentally</td>
<td>103.1</td>
</tr>
<tr>
<td>Kandlikar's CHF Model without light</td>
<td>143.9</td>
</tr>
<tr>
<td>Kandlikar's CHF Model with light</td>
<td>150.2</td>
</tr>
<tr>
<td>Zuber's CHF Model</td>
<td>107.0</td>
</tr>
</tbody>
</table>

Boiling experiments on smooth CVD titanium dioxide surface have proven to indicate a change in boiling performance under the influence of UV light due to a chemical mechanism. Future studies are needed to minimize contamination and also to potentially speed up the process of increasing hydrophilicity by means of micro- and nano-structuring, or in combination with hydrophobic patterning.

4.1.3. Carbon Nanotubes

The CNT deposition performed by Arun Kousalya from Purdue University yielded a randomly oriented multi-walled carbon nanotube forest characterized by vastly different cavity sizes and orientations. Two SEM images accompanied with an initial XPS survey spectrum is show in Figure 34. SEM imaging indicates a randomly oriented array with varying diameters of the nanotubes from tens of nanometers to as large as a micron. The XPS spectrum exhibits predominately carbon and oxygen peaks. This is to be expected as oxygen molecules tend to become bound to the CNT matrix at defect sights in the absence of hydroxyl groups. Overall, the substrates themselves appear to be
a very clean, well deposited CNT network with randomly oriented arrays of several different length scales.

Figure 34: CNT a) SEM image of pre-boiled sample; b) High magnification image of CNT arrays; and c) XPS Spectra of CNT sample

Carbon nanotube samples were examined using the same procedures used with titanium dioxide for comparison purposes. Set 1 experiments to investigate changes in
HTC and ONB upon UV irradiation and Set 2 experiments to determine changes in CHF were performed on the CNT samples. Four separate samples were used in CNT experiments, and the sample matrix can be seen in Table 7.

Table 7: CNT sample testing database

<table>
<thead>
<tr>
<th>CNT Samples</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Extended long-term boiling tests under water immersion and UV irradiation</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Contact angle experiments performed on sample subjected to same water immersion and UV irradiation times as Sample 1</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Boiling test to CHF without light</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Boiling test to CHF with light irradiation for 48 hours</td>
</tr>
</tbody>
</table>

Carbon nanotube Sample #1 was used to observe changes in HTC and ONB temperature upon boiling and UV-light exposure. Boiling runs 1-3 were performed without exposure to UV-light to determine the changes in boiling parameters due to the boiling process alone. Runs 4-6 were run under varying irradiation times, and the final Run 7 was left in darkness. A detailed outline of sample Runs 1-7 can be seen in Table 8. The fully developed nucleate boiling curve from a heat flux of 40 W/cm² to 70 W/cm² is shown in Figure 35 and the complete boiling curve can be seen in Appendix B. The heat transfer coefficient values of these boiling runs are plotted in Figure 36.
Table 8: Description of testing procedure for CNT Sample 1

<table>
<thead>
<tr>
<th>Run #</th>
<th>Description of CNT Testing Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>Sample placed in apparatus in darkness with water, left 24 hours then began boiling run</td>
</tr>
<tr>
<td>Run 2</td>
<td>Water drained immediately after Run 1, refilled, and sample kept in apparatus in the dark after Run 1, and boiling run began 24 hours later</td>
</tr>
<tr>
<td>Run 3</td>
<td>Water drained immediately after Run 2, refilled, and sample kept in apparatus in the dark after Run 1, and boiling run began 4 hours later</td>
</tr>
<tr>
<td>Run 4</td>
<td>Water drained immediately after Run 3, refilled, and lamp turned on at 500W, boiling run began 20 hours later</td>
</tr>
<tr>
<td>Run 5</td>
<td>Water drained immediately after Run 4, refilled, and lamp kept on at 500W, boiling run began 4 hours later (24 hours of light irradiation)</td>
</tr>
<tr>
<td>Run 6</td>
<td>Water drained immediately after Run 5, refilled, and lamp kept on at 500W, boiling run began 24 hours later (48 hours of light irradiation)</td>
</tr>
<tr>
<td>Run 7</td>
<td>Water drained immediately after Run 7, refilled, lamp turned off and sample kept in darkness for 120 hours, then boiling run began</td>
</tr>
</tbody>
</table>

Figure 35: Nucleate pool boiling data for CNT Sample 1
Figures 36: HTC change from CNT boiling experiments under light exposure.

Runs 1, 2, and 3 show a decrease in HTC with boiling without light exposure. Once the lamp is initiated, a sudden HTC increase of 14.5% to slightly over 9.3 W/cm²°C is observed. The increase in HTC observation is similar to that of Kousalya on the same CNT surfaces, however, it is less of a change due primarily to the fact that these CNT films are deposited on a smooth surface. As the boiling tests continue and the sample is exposed to a greater amount of UV irradiation, the HTC decreases by 6.2%. After the sample is left in darkness for an extended period of time, the HTC decreases by 8.1% and appears to revert back to the initial pre-irradiation surface conditions.

SEM analysis of the sample before and after boiling reveals a degradation of the CNT array due to the boiling process. A significant amount of the exposed area of CNTs has been compacted to form a more highly dense network. This is a driving factor in the decrease in heat transfer coefficient seen in the boiling tests, as the number of active nucleation sites and areas for capillary wicking is significantly decreased. The upper layers of CNTs seem to be less adhered to the surface than the underlying base layer.
is important to note that the water was drained after each experiment to prevent nanofluid suspension in the liquid. XPS analysis was used after Run 7 and determined that carbon was still the predominant species on the surface, with a slight increase in oxygen concentration on the surface with only a tiny titanium contribution that could be due to the underlying catalyst layer. Both SEM images and XPS survey spectra can be seen in Figure 37.

Figure 37: CNT post boiling surface analysis a) SEM image of CNT degradation; b) High resolution SEM image of CNT post-boiling; and c) XPS spectra of pre- and post-boiling samples
Contact angle experimentation shows virtually no change in contact angle under water immersion and darkness. The lamp was turned on to a power of 500W and contact angle tests were performed at 20, 24, and 48 hours of irradiation. Following the last test, the sample was left in the apparatus and left in the dark for 100 hours. A decrease in contact angle to less hydrophobic surface energy upon UV irradiation is observed, with an almost complete reversion to the initial superhydrophobic state prior to light exposure. The results of the contact angle tests can be seen in Figure 38. The increase in HTC with a decrease in contact angle is the opposite trend of what is typically seen on a smooth surface. The structural wicking of the nanotube structure increases the liquid flow to the surface via capillary action, and increases the HTC.

![Graph showing contact angle results on CNT Sample #2](image)

**Figure 38: Contact angle results on CNT Sample #2**

Set 2 experiments on Sample 3 and 4 were used to examine changes in CHF of the CNT arrays under UV irradiation. Sample 3 was left in the dark under water immersion and Sample 4 was irradiated for 48 hours with UV-visible light. The boiling
curves to CHF can be seen in Figure 39. A significant increase in CHF upon light irradiation from 97.1 W/cm² to 121.6 W/cm² is due to the change in wettability to a more hydrophilic surface energy upon exposure to light. As CHF is about to be reached, the increased wicking forces of the more hydrophilic irradiated CNT arrays increases liquid replenishment to the surface by capillary pumping, and thus delaying the CHF condition.

![Figure 39: CHF results of CNT boiling tests with and without light exposure](image)

The models used to predict CHF do not incorporate surface roughness in the model generation and thus the nanotube structuring will drastically effect the predictions. Experimental values compared to modeling results can be seen in Table 9. Kandlikar’s model for CHF predicts an increase in CHF value with increase in hydrophilicity, trending well with the experimental results. However, the values of Kandlikar’s method prediction are significantly lower than the actual boiling results. This reiterates the importance of surface structuring in boiling studies. Just by structuring the surface of a material, an order of magnitude increase in boiling CHF value is measured.

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experimentally without light exposure. Zuber’s model does not accommodate for surface roughness and is dependent upon the phase change liquid, and thus provides a value again of 107.0 W/cm$^2$, which is in fairly good agreement with experimental results. There has yet to be a comprehensive model for nanotubes that predicts the CHF within an acceptable error. Extensive studies are necessary to generate a model of this type based on surface energy.

<table>
<thead>
<tr>
<th>Description</th>
<th>CHF Value (W/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT without light, measured experimentally</td>
<td>97.1</td>
</tr>
<tr>
<td>CNT with light, measured experimentally</td>
<td>121.6</td>
</tr>
<tr>
<td>Kandlikar's CHF Model without light</td>
<td>7.4</td>
</tr>
<tr>
<td>Kandlikar's CHF Model with light</td>
<td>40.4</td>
</tr>
<tr>
<td>Zuber's CHF Model</td>
<td>107.0</td>
</tr>
</tbody>
</table>

CNT arrays, deposited by means of microwave plasma chemical vapor deposition, have proven to be significantly affected by boiling under UV-visible light exposure. After 48 hours of light exposure, an increase in HTC and CHF is observed. If these arrays are to be incorporated in active thermal control systems, mechanisms to speed up hydrophilic conversion time and superhydrophobic reversion time are necessary.

### 4.2. Electrochemical Results on Copper

Electrochemistry tests were performed on three separate bare roughened copper substrates to CHF, as outlined in the procedure from Section 3.2.5. Boiling curves can be seen in Figure 40. The results indicate a significant variance in CHF values occurs among Run 1, 2, and 3. Run 1 has a significantly lower critical heat flux value and superheat temperature than Runs 2 and 3. Typical values for roughened copper in ultrapure water have been reported by Hunter et al.\cite{50} and are near 90 W/cm$^2$. This study
is slightly different however, in that the same sample preparation techniques were used but the electrolyte was a low concentration sodium chloride solution instead of ultrapure water. The HTC seems to be fairly similar in all three cases, but a slightly higher heat transfer coefficient occurs in the first run.

![Saturated pool boiling curves for roughened copper in 0.005M NaCl solution](chart)

**Figure 40:** Saturated pool boiling curves for roughened copper in 0.005M NaCl solution

As heat flux and superheat temperature increase throughout the boiling experiment, the impedance increases as well. This is likely due to the increase in substrate surface area covered by vapor, which has a higher impedance to current flow as compared to liquid. As the heat flux was increased and more vigorous nucleate boiling was evident, vapor covered more of the substrate and impeded charge transfer more
significantly. The magnitude of the impedance vector, |Z|, at different steady state boiling points is illustrated in Figure 41.

![Figure 41: Change in the steady state impedance vector magnitude value at 1000 Hz during pool boiling tests](image)

The phase angle exhibited a slight decrease over time during nucleate boiling from an average value of -0.79° to -2.26°. This phase angle decrease corresponds to an increase in the imaginary component of the impedance, indicating a slightly greater contribution to the impedance is now due to the capacitive circuit element.

Despite the range of CHF values, a relation between CHF and the impedance magnitude immediately prior to CHF is evident. All three runs experience a „critical impedance“ between 1.85 kΩ-cm² and 2.35 kΩ-cm². Thus, the critical impedance parameter appears to be a predictor of CHF in these experiments, regardless of the heat flux value at which it occurs. Such a signature for CHF enabled by a relatively simple electrochemical measurement could potentially be useful in many practically boiling
technologies. Predictive measures for pool boiling CHF have been investigated intently\textsuperscript{64,89-91}, but none have incorporated an electrochemical perspective into a predictive method for this phenomena.

Bubble formation rate and bubble size increase with heat flux, giving rise to more required liquid replenishment to the substrate surface to maintain the same heat transfer rates. Eventually, upon reaching CHF, a vapor film forms over the entire surface and severely impedes liquid replenishment. The impedance value jumps two orders of magnitude at this film boiling transition point due to the lower electrical conductivity of current through the vapor film. Impedance and phase angle changes from a steady state nucleate boiling regime to a transient unstable film boiling regime can be seen in Figure 42. Surface oxide layer formation due to the exposure to high temperatures must also be considered and could be contributing to this initial spike, but the assumption to this analysis was that the high impedance was predominantly caused by the vapor layer.

Upon the sudden realization of CHF, a significant phase angle change in the impedance signal from about -2.5 up to -30 degrees is evident, indicating a sudden increase in the overall capacitance. At this sudden change in surface interface conditions there is both an increased resistance to electron flow and charge stored in the vapor layer as useful energy in the form of capacitance.
Unstable film boiling is a complex and poorly understood process. Westwater\textsuperscript{63} describes transition boiling as a regime that is neither nucleate or film boiling, but somewhere in between. The water vapor blankets the entire surface and no liquid-solid contact occurs in this regime, but the film is rough and unstable. Westwater observes, using a photographic study, that immediately following CHF, the boiling is characterized by violent plumes of vapor as the liquid tries to penetrate to the hot surface. These violent explosions decrease as the film becomes more stable. Others, including Bankoff\textsuperscript{23}, theorize that a periodic quenching of liquid with the solid surface occurs. The theory stems from the fact that because solid surface characteristics play such an important role in the transition boiling heat transfer, surface effects must come into play and therefore liquid must be in contact with the surface at some point. Rajabi\textsuperscript{77} observed,
using electrochemistry, that there is some liquid solid contact at critical heat flux, but this phenomena does not account for the total extent of current transport in this regime. A wetted area of around 65% was reported, and the heat flux was proven to fall much faster than the surface contact area.

A slow exponential decrease in impedance over time after an initial sharp increase would imply that current is able to flow through the vapor film easier than at the onset of transition boiling. As the temperature increases and transient heat flux continues to decrease, the film becomes less violent and more stable due to the increasing thickness of the vapor layer. The electrochemistry data leads to the conclusion that the stability of the film is the process that controls the impedance response. Once the film is stable enough, the transient heat flux increases again into stable film boiling, where radiation effects are dominant.

The complete evaluation of this data after the initial CHF spike would require incorporating optical techniques to explain boiling phenomena, and a more detailed understanding of the mechanisms behind the transition boiling regime could be achieved.
CHAPTER V

CONCLUSIONS AND FUTURE WORK

Extensive pool boiling studies have been conducted to investigate changes in critical boiling parameters and fundamental mechanisms behind photonic excitement of surfaces under boiling conditions. Samples of copper, titanium dioxide, and CNTs provided a framework for a comprehensive photonically enhanced and controlled boiling study.

Results on copper substrates reveal both a chemical and physical change to the boiling surface. An increase in Cu$_2$O formation on the surface in the form of nanoclusters gave way to an induced 35% decrease in CHF upon light irradiation. A hypothesis has been presented that the decomposition of copper hydroxide and formation of Cu$_2$O leads to a decrease in surface temperature that initiates the CHF condition.

Titanium dioxide thin films deposited by means of reactive sputtering deposition were also investigated for use in UV irradiated boiling experiments. A significant change in superhydrophilicity seen in the contact angle experiments of 55.3% correlated to a 16.8% decrease in HTC in boiling studies. Contact angle testing determined the surface failed to revert to the initial pre-boiling surface energy state even after 100 hours of darkness, and the HTC value from the boiling experiment did not revert as well. CHF testing of UV light exposed titanium dioxide did not yield a significant change in heat flux value.
Multi-walled CNT arrays deposited by means of microwave plasma chemical vapor deposition (MPCVD) were investigated for use in actively controlled pool boiling studies. An increase in hydrophilicity with irradiation time is observed through small scale contact angle tests with the ability to fully revert within 100 hours. Boiling on the CNT samples resulted in a morphology change to a higher density nanotube forest, and results indicate an increase in HTC and CHF upon light irradiation. Correlating well with the contact angle experiments, the HTC of the nanotube array reverted to the initial conditions in the absence of light energy.

The desire to actively measure the liquid solid contact on the surface during boiling procedures sparked an interest in using electrochemical techniques to measure impedance. These techniques have been demonstrated before, but a new technique that does not affect surface conditioning is presented. Boiling results on copper without the presence of UV irradiation indicate a potential predictive method to determine CHF. A critical impedance range of 1.85 kΩ-cm$^2$ and 2.35 kΩ-cm$^2$ is observed to contain the CHF condition regardless of heat flux. The results provide additional insight into CHF mechanisms and fundamental boiling phenomena.

The control of surface energy by use of light energy has proven to directly affect boiling performance of photoactive surfaces. Future studies are recommended to create surfaces that provide an increase of several orders of magnitude in conversion and reversion times with light energy. Photocatalyst that exhibit conversion times on the order of seconds or minutes would be imperative to real-world applications. Also, patterned surfaces with multiple photocatalytic materials could optimize active thermal control and provide for additional multi-phase heat transfer enhancement.
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APPENDIX A

ROHSENOW MODEL FOR HEAT TRANSFER

Rohsenow developed a heat transfer model in the early 1950s based on the postulation that heat flows from the surface first to the adjacent liquid similar to a single-phase convection process. He then postulated that a single phase model for heat transfer coefficient can be adopted for multi-phase with some slight adjustment and the appropriate length and velocity scales.

The discussion begins with the typical Nusselt correlation:

\[ \text{Nu}_b = \frac{hL_b}{k_l} = A\text{Re}_b^n \text{Pr}_l^m \]

the Reynolds number associated with the bubble formation, \( \text{Re}_b \) is given by:

\[ \text{Re}_b = \frac{\rho_v U_b L_b}{\mu_l} \]

Rohsenow then took the length scale, \( L_b \), and velocity scale, \( U_b \), to be the departure diameter \( d_d \) and the vapor superficial velocity:

\[ L_b = d_d = C_b \theta \left[ \frac{2\sigma}{g(\rho_l - \rho_v)} \right]^{1/2} \]

\[ U_b = \frac{q^*}{\rho_v h_{tv}} \]
where $\theta$ is the contact angle, $C_b$ is a constant that is specific to the system conditions, and $h_{lv}$ is the latent heat of vaporization of the liquid. Newton’s law of cooling is then used to simplify the expression:

$$h = \frac{q^*}{T_w - T_{sat}}$$

The relationship between the Nusselt number and the Reynolds and Prandtl number is suggested by Rohsenow to take the form

$$Nu_b = AR\varepsilon_b^{(1-r)}Pr_l^{(1-s)}$$

After some simplification, the Rohsenow correlation yields

$$\frac{q^*}{\mu_l h_{lv} \left[ \sigma \frac{g}{(\rho_l - \rho_v)} \right]^{1/2}} = \left( \frac{1}{\mathcal{C}_{sf}} \right)^{1/r} Pr_l^{s/r} \left[ \frac{C_{ptl}[T_w - T_{sat}]}{h_{lv}} \right]^{1/r}$$

where

$$\mathcal{C}_{sf} = \frac{\sqrt{2} C_b \theta}{A}$$

Rohsenow recommends a value of $s = 1.0$ and $r = 0.33$ for water.

Vachon$^{93}$ used literature results to tabulate $C_{sf}$ based on fits from the pool boiling literature. The values can be seen in Table 10.

<table>
<thead>
<tr>
<th>Liquid-surface combination</th>
<th>$C_{sf}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water on Teflon pitted stainless steel</td>
<td>0.0058</td>
</tr>
<tr>
<td>Water on scored copper</td>
<td>0.0068</td>
</tr>
<tr>
<td>Water on ground and polished stainless steel</td>
<td>0.0080</td>
</tr>
<tr>
<td>Water on emery polished copper</td>
<td>0.0128</td>
</tr>
<tr>
<td>Water on chemically etched stainless steel</td>
<td>0.0133</td>
</tr>
<tr>
<td>Water on mechanically polished stainless steel</td>
<td>0.0132</td>
</tr>
<tr>
<td>Water on emery polished, paraffin-treated copper</td>
<td>0.0147</td>
</tr>
</tbody>
</table>
One of the major disadvantages of this method is that experiments must be conducted to determine the $C_{sf}$ of a particular combination. If the combination of interest cannot be found in these tables, it is suggested that a value of 0.013 should be taken as a first approximation. For experiments where change in contact angle is important, a liquid-surface combination experiment to determine $C_b$ is of great value.

Rohsenhow’s model for predicting heat transfer coefficient was used to estimate heat transfer rates of CNT arrays and titanium dioxide films. The analysis and steps to incorporate the model are strongly dependent on $C_b$, the coefficient used to incorporate contact angle. Modeling was attempted on the titanium dioxide thin films and was unsuccessful in creating a comprehensive value for $C_b$. Likewise, CNT samples exhibit the opposite trends predicted in this heat transfer model and therefore were not considered in predicting HTC. In future studies, if an accurate value for $C_b$ can be determined that applies for a wide range of contact angles, this model could be a significant asset in surfaces that change wettability.
APPENDIX B

BOILING CURVES FOR TiO2 AND CNT SAMPLES

Figure 43: Full pool boiling test for TiO2 Sample 1
Figure 44: Full pool boiling test for CNT Sample 1