

THE EFFECT OF SURFACE WETTABILITY ON FAST TRANSIENT MICROBOILING BEHAVIOR

Owen Thomas, Richard E. Cavicchi, and Michael J. Tarlov

Chemical Science and Technology Laboratory

National Institute of Standards and Technology

Gaithersburg, Maryland 20899

ABSTRACT

Microboiling events associated with the fast transient heating of a micrometer-scale metallic thin film heater immersed in water have been studied. The effect of surface properties on the microboiling transients was examined by modifying heater surfaces with hydrophobic and hydrophilic alkanethiol self-assembled monolayers (SAMs). The microheaters are thin films of platinum or gold-plated platinum that are approximately tens of microns in width and hundreds of microns in length. The micro-heaters are immersed in water and rapidly heated with short ($<10\ \mu\text{s}$) square voltage pulses. The temperature-time transients of the micro-heaters are obtained by measuring the heater resistance during the application of the heating pulse. The bubble nucleation event associated with boiling is signaled in the temperature-time transient by an inflection point that results from a change in heat transfer when a vapor bubble forms on the heater. Because of the extremely high heating rates ($>10^8\ \text{K/s}$), superheating occurs and nucleation temperatures as high as $296\ ^\circ\text{C}$ have been measured in water. The surface of gold-plated heaters were coated with a series of hydrophilic [$\text{HO}(\text{CH}_2)_6\text{SH}$, $\text{HO}(\text{CH}_2)_{11}\text{SH}$, $\text{HO}(\text{CH}_2)_{16}\text{SH}$] and hydrophobic [$\text{CH}_3(\text{CH}_2)_7\text{SH}$, $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, and

CH₃(CH₂)₁₅SH] SAMs. Dramatic differences are observed in the temperature-time transients of hydrophilic versus hydrophobic SAM-coated microheaters. Microheaters modified with hydrophobic SAMs exhibit lower boiling nucleation temperatures, more pronounced inflection points, and higher average temperatures during microboiling. These differences can be rationalized by considering simple models of surface wetting and surface vapor bubble formation.

In this paper we describe experiments of fast transient microboiling from rapidly heated metal lines immersed in water. Using alkanethiol self-assembled monolayers (SAMs) to modify the heater surface, we demonstrate that microboiling is sensitive to the surface wetting properties of the heater. The metal lines are Pt or Au-modified Pt thin films, approximately 200 nm thick and 3 x 200 μ m in dimension, that act as fast transient microheaters when subjected to short (<10 μ s) voltage pulses. With sufficient applied voltage, water in close proximity to the microheater is heated to a high enough temperature to cause nucleation of a vapor bubble on the surface. In other words, boiling occurs. Because of the small size of the metallic features and the rapid heating rate used, boiling events are confined to the near surface region of the microheater. We therefore term this microboiling. We use a method similar to that first reported by Avedisian to obtain temperature-time transients of the microheaters.¹ By measuring the heater's resistance during heating, a temperature-time profile of the heater is obtained. As in prior studies we find that the nucleation of a vapor bubble, i.e., the onset of boiling, is signaled in the transient by an inflection point. To our knowledge this is the first study using well-defined surfaces of known chemical functionality to examine boiling phenomena.

There have been several recent studies of boiling at rapidly heated microstructures immersed in liquids.¹⁻⁸ Typically in these experiments, metallic thin films or wires of micrometer dimensions are immersed in a liquid and heated resistively with a short voltage pulse lasting 2 μ s to 20 μ s. These studies have been performed to both understand the fundamental science underlying this phenomenon and to exploit the effect for practical applications. For example, bubble nucleation at rapidly heated thin metallic films is the basis for ink-jet printing. Ink droplets are ejected through a small orifice by the growth of expanding microbubbles formed at the surface of a lithographically patterned microheater. The low thermal mass of the microheaters allows for resistive heating and concomitant rapid boiling on a time-scale of microseconds. In a conceptually similar process, others have explored the feasibility of using the kinetic energy of rapidly expanding bubbles to drive micromechanical systems.^{9,10} Although ink-jet printing is a pervasive and robust technology, a fundamental understanding of the mechanisms, thermodynamics, and fluid dynamics of rapid bubble nucleation still has not been developed.

Avedisian's group examined the fast resistive heating of thin film heater elements used in ink-jet printing.¹ Ta/Al thin films, $\sim 65 \mu\text{m}$ on a side, were immersed in water and resistively heated by subjecting them to short, microsecond time-scale, voltage pulses. The average surface temperature of the Ta/Al heating elements was determined by essentially using the thin film as a thermistor. An inflection point in the temperature-time transients was observed that was assigned to the bubble nucleation event. They determined that the high heating rates ($\sim 10^8 \text{ K/s}$) lead to superheating of the water well above its boiling point. Nucleation temperatures up to 282°C were determined at the

highest heating rates. They also suggested that homogeneous nucleation at a surface is the mechanism for bubble formation based on reasonable agreement between measured nucleation temperatures and those predicted by homogeneous nucleation theory.

In a more recent report, Poulikakos's group used a method similar to that devised by Avedisian to study bubble nucleation on pulsed, resistively heated 10 μm diameter Pt wires.³ They termed the bubble nucleation process arising from the rapidly heated wires "microscale explosive vaporization." In addition to temperature measurements, strobe microscopy and fast pressure transduction were used to obtain visual images of bubble nucleation and to measure the acoustic emission of expanding bubbles, respectively. Using both temperature and pressure measurements, they were able to estimate the pressure inside growing bubbles and the mechanical energy released by bubble expansion that might be used to perform work in MEMS devices.

Here, we describe the use of fast transient bubble nucleation for probing the wetting properties of surfaces. Our study was motivated by two considerations. First, nucleation theory predicts that the nucleation temperature will vary with contact angle or surface wettability.¹¹ While it has been long known that surface wetting properties can influence the critical heat flux observed in steady-state pool boiling¹²⁻¹⁴, we believe that the work presented here is the first systematic study of the effect of heater surface condition on fast transient microboiling behavior using SAMs. We demonstrate that microboiling behavior can be dramatically altered by changing the terminal functional group of alkanethiol SAMs formed on a microheater surface.

EXPERIMENTAL

Overview: The experiments described in this section consist of two discrete studies. The

first study involves determining the variation of nucleation temperature with heating rate of a bare platinum heater. This study is similar to that performed by Avedisian and coworkers using ink-jet printer heads and was undertaken to validate our methods of temperature determination and calibration.¹ The second study examines the effect of microheater surface wetting properties on bubble nucleation. Here the temperature-time profiles are obtained of gold plated platinum heaters whose surfaces are made either hydrophobic or hydrophilic by coating with n-alkanethiol or hydroxyl-terminated alkanethiol SAMs, respectively.

The Heater: A micrograph of one of the micro-scale heaters employed in this study is shown in Figure 1. The thin film heaters were fabricated at Lincoln Laboratories and consist of a 200 nm thick layer of platinum on top of a 30 nm thick titanium adhesion layer. The heater is deposited on a 0.2 μm SiO_2 layer on Si. The oxide layer thermally isolates the heater and is necessary to observe the inflection point in the heating transient that signals the bubble nucleation event. The heaters were diced from the silicon wafers and mounted in a 40-pin dual inline package. Wire bonds, visible in the micrograph, were used to electrically connect the heater to the package. The straight-line portions of the heater, which were used in our experiments, are indicated in Figure 1 by arrows. The width of the heater line is 3 μm , and the length of the portions used for heating is approximately 200 μm . The room temperature resistance of the platinum heater line employed in the presented heating rate study was 55.7 Ω .

Preparation of Gold and Thiolated Gold Surfaces: For the studies of self-assembled monolayers on gold surfaces, a platinum heater like the one described above was

electroplated with gold. Plating was performed by submerging the platinum heater in Bright Electroless Gold solution (Transene Co.)* and biasing the heater surface to -2 V relative to ground. The plating process was visually monitored through an optical microscope and was typically stopped within 3 minutes. The room temperature resistance of the gold-coated heater used in the presented monolayer study was 32.7 Ω . Using the bulk resistivities for gold and platinum, the thickness of the gold layer on this device is estimated to be about 35 nm.

SAMs of n-alkanethiols [$\text{CH}_3(\text{CH}_2)_7\text{SH}$, $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$] and hydroxyl-terminated alkanethiols [$\text{HO}(\text{CH}_2)_6\text{SH}$, $\text{HO}(\text{CH}_2)_{11}\text{SH}$, $\text{HO}(\text{CH}_2)_{16}\text{SH}$] were formed on gold heater surfaces by pipetting of ~ 1 mM thiol-ethanol solution on the chip surface and incubating for 25 min. The heater surface was then thoroughly rinsed with ethanol and blown dry with compressed air. The dry, monolayer-covered heater was then immersed in de-ionized water (75 ml) and submitted to a series of heating pulses. (See **Heating and Measurement** section below.) To clean the heater surface for assembly of another alkanethiol monolayer following heating experiments, the heater was removed from the de-ionized water, rinsed with ethanol, and UV-Ozone cleaned for 20 minutes. The clean heater was then prepared with the next thiol solution of interest. In addition, heaters cleaned using this procedure are referred to as “bare” Au and were used to obtain temperature-time profiles of ostensibly clean Au surfaces. Hydrophobic and hydrophilic monolayers were prepared in an alternating fashion, and the exact order of monolayer preparation for the data presented in this study is as follows: 1) $\text{HO}(\text{CH}_2)_{16}\text{SH}$, 2) $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$, 3) $\text{HO}(\text{CH}_2)_6\text{SH}$, 4) $\text{CH}_3(\text{CH}_2)_7\text{SH}$, 5) $\text{HO}(\text{CH}_2)_{11}\text{SH}$, 6) $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$.

Heating and Measurement: In our experiment, the micro-scale heater functions

simultaneously as heater and thermometer. The temperature of the heater is determined by measuring the change in resistance of the heater during a heating pulse. In a separate procedure described in detail below, a plot of heater resistance vs. temperature is obtained. This plot serves as a temperature calibration for the heating pulses.

A schematic of the experimental setup is shown in Figure 2. The rapid heating of a micro-scale heater was achieved by applying square voltage pulses to a Wheatstone bridge, one leg of which was the heater itself. The voltage pulses were generated by a pulse generator (Agilent 8114A)*. For the study of heating rates of bare platinum heaters, voltage pulses were applied to the bridge at 10 Hz, and were varied in magnitude from 7.4 V to 10.4 V and in duration from 2 μ s to 8 μ s. For the study of thiolated gold surfaces, pulses of 7.2 V and 5 μ s duration were applied at a frequency of 2 Hz. It should be noted that the heaters used in these studies have been experimentally observed to return to room temperature within 20 μ s of the termination of the applied voltage pulse.

To determine the temperature response of the heater to an applied voltage pulse, the voltage difference between probe points A and B on Figure 2 (V_{out}) was measured with a fast differential probe (Lecroy AP033)*. The output of this probe was connected to a digital oscilloscope (Lecroy LT264)*, which was triggered by the input heating pulse. The time window captured by the oscilloscope was set to display V_{out} vs. time for the entire pulse duration, and the captured V_{out} vs. time waveforms were sent through a GPIB interface to a computer, where they were stored.

Before using the experimental setup to obtain an actual temperature response of the heater, one must go through a procedure to balance the Wheatstone bridge. This is

accomplished by applying small voltage pulses ~ 1 V to the circuit and adjusting the potentiometer R_3 until V_{out} is negligible in magnitude. The thin film heaters used in this study undergo a decrease in room temperature resistance R_{HI} of approximately 10 % with initial thermal stressing. This decrease requires that the heaters be taken through a “burn in” procedure prior to being used for actual temperature measurements. This procedure involves iteratively heating and rebalancing the Wheatstone bridge until no further changes in resistance are observed. Once burn in of the heater is complete, R_{HI} is measured with a digital ohmmeter and recorded.

Referencing Figure 2 and assuming a balanced bridge, the relationship between the measured voltage V_{out} and the real time resistance of the heater R_H can be derived as follows:

$$V_{out} = V_A - V_B = V_{in}R_H/(R_H + R_1) - V_{in}R_3/(R_3 + R_2) \quad (1)$$

Letting $R_3 = R_{HI}$, $R_1 = R_2$ and rearranging:

$$V_{out} = V_{in}(R_H/(R_H + R_2) - R_{HI}/(R_{HI} + R_2)) \quad (2)$$

Solving for the real time heater resistance R_H one obtains:

$$R_H = R_2/(1/(V_{out}/V_{in} + R_{HI}/(R_{HI} + R_2)) - 1) \quad (3)$$

The above equation relates R_H to V_{out} , which is directly measured. To convert R_H to heater temperature T_H , one must determine the thermal coefficient of resistivity θ for the heater of interest. R_H is related to T_H through the following relationship:

$$R_H = R_{HI} + R_{HI}\theta(T_H - T_{HI}) \quad (4)$$

Where R_{HI} and T_{HI} are the initial temperature and resistance of the heater. (In our experiment $T_{HI} = 22\text{ }^{\circ}\text{C}$.) The thermal coefficient of resistivity θ was obtained for the heaters by monitoring their resistance during application of a gradual temperature ramp. The heaters were placed in a tube furnace (Thermolyne Type 21100)* and heated gradually from room temperature to $\sim 300\text{ }^{\circ}\text{C}$. Temperature was measured using a Chromel-Alumel thermocouple, and resistance measurements were taken at 10° intervals. Figure 3 is a plot of R_H / R_{HI} vs. temperature for both the platinum- and gold-coated platinum heaters employed in this work. A linear least-squares fit was applied to the data, and the slopes of the fitted lines, which are by definition the thermal coefficients of resistivity, were determined to be $0.00250\text{ }^{\circ}\text{C}^{-1}$ and $0.00209\text{ }^{\circ}\text{C}^{-1}$ for the platinum and gold coated platinum heaters respectively. Using the determined thermal coefficient of resistivity, the temperature of a heater may be calculated by the relation:

$$T_H = (R_H / R_{HI} - 1) / \theta + T_{HI} \quad (5)$$

Substituting equation 3 above for R_H results in the following expression for the determination of T_H from V_{out} .

$$T_H = (R_2 / (1 / (V_{out} / V_{in} + R_{HI} / (R_{HI} + R_2)) - 1) / R_{HI} - 1) / \theta + T_{HI} \quad (6)$$

In the experiments presented here, all data were obtained directly as V_{out} vs. time waveforms, which were subsequently converted to T_H vs. time.

The cooldown process after a pulse may be monitored by using a small DC offset voltage added to the pulse, and measuring the resistance change after the pulse. With pulses of the amplitudes and duration mentioned above, the heaters return to room temperature well within 20 μ s of the termination of the applied voltage pulse. The cooldown timescale is thus much faster than the time between pulses. For the rest of the experiments described here, the DC offset was zero.

RESULTS

General Features of Temperature vs. Time Waveforms

Figure 4 shows a typical plot of temperature vs. time for a platinum heater, to which a voltage pulse of 6.7 V was applied for 13 μ s. This figure illustrates the general characteristics of a temporal heating profile for a rapidly heated microheater immersed in liquid. The heating profile can be considered to have three distinct regions: pre-boiling, boiling, and oscillatory. The pre-boiling region represents the initial heating of the microheater, which precedes the growth of gas phase nuclei on the heater surface. Within the pre-boiling region, the temperature of the heater increases in an exponential fashion, with the heating rate, defined as $d(Temperature)/d(time)$, decreasing with time. The pre-boiling region ends at the first point on the temperature vs. time waveform where $d^2(Temperature)/d(time)^2 = 0$. This inflection point is marked by an “X” in Figure 4 and indicates the onset of bubble growth on the heater surface. The temperature at the inflection point is referred to as the nucleation temperature. The boiling region, which immediately follows the inflection point, is characterized by an exponential increase in heater temperature similar to that observed in the pre-boiling region. This temperature

increase is associated with the continued growth of vapor-phase nuclei on the heater surface. When vapor bubbles grow, the solid surface comes into increasing contact with the vapor phase. As a consequence of the vapor's lower thermal conductivity relative to liquid, a rapid rise in heater temperature results. Following the boiling region is an oscillatory region characterized by periodic decreases in the heater temperature. The oscillatory region is interpreted as being the consequence of repeated bubble formation and collapse at the heater surface and will not be considered further in this work.¹ In the experimental studies presented in this paper, heating pulses were limited in width to avoid the oscillatory region.

In an earlier study, Avedisian and coworkers interpreted inflection points, such as the one indicated in Figure 4, as signifying the onset of nucleation at the surface of ink-jet printer heads.¹ Subsequent studies by Glod and coworkers correlated the assignment of onset of nucleation by this method with the onset of nucleation observed through high-speed microscopy and acoustic pressure measurements.³ The basis for the inflection point may be understood in terms of a simple physical model. Prior to nucleation, the temperature of the heater increases in an exponential manner, with the heating rate decreasing as the rate of heat transfer from heater to surroundings, in this case the substrate and water, approaches the rate of heat generation. This behavior is consistent with the heater being described by a lumped capacitance¹⁵ model and has been described as such by Avedisian and coworkers.¹ In this model, the temperature of the heater is assumed to be uniform, and the rate of heat transfer from heater to surrounding fluid is proportional to both the **wetted** area of the heater and the temperature difference between heater and liquid. When bubble nucleation or microboiling occurs, vapor nuclei displace

liquid at the heater surface, resulting in a decrease in the wetted area of the heater. Because the thermal conductivity of a vapor is typically much lower than that of the liquid, a significant increase in heating rate is observed. In a plot of heater temperature vs. time, this increase in heating rate is manifested as an inflection point.

It should be noted that the nucleation temperature (273 °C) for the heater in Figure 4 far exceeds the saturation or boiling temperature of water at atmospheric pressure, i.e., the water immediately adjacent to the heater is significantly superheated prior to bubble formation. Such superheating is typical of boiling occurring on rapidly heated surfaces. For a completely wetting surface, it is expected that the superheat associated with the boiling liquid will increase with increasing heating rate up to the so-called “theoretical limit of superheat”.¹⁶ For most liquids, including water, the theoretical limit of superheat is close to the critical temperature.¹¹

Heating Rate Study

To confirm that our procedures for temperature calibration and nucleation temperature determination provide results consistent with previous studies of bubble nucleation on transiently heated surfaces, we examined the evolution of nucleation temperature as a function of heating rate. Figure 5a shows the experimentally determined heating profiles of a platinum heater to which voltage pulses of varying magnitude and duration have been applied. Figure 5b shows the first derivatives of these heating profiles with respect to time. Inflection points are indicated by an “X” on each heating profile and associated derivative, and were determined by locating the minimum value for dT/dt on each graph in figure 5b. When more than one inflection point is evident in the derivative

graph, as is the case for the 6.5 volt heating pulse, the inflection point that immediately precedes the rapid increase in heating rate is assigned as representing the true onset of bubble nucleation. This assignment is based on the rationale that nucleation occurring over a significant fraction of the heater surface will result in a large increase in total surface temperature whereas a localized nucleation event may result in a small, short-duration increase in surface temperature.

In order to reduce the noise inherent in the derivative curves, significant smoothing of both the heating transients and their derivatives was performed. The heating transients were smoothed using a symmetric Savitsky-Golay method, in which a second order polynomial was used and each data point was smoothed relative to 10 adjacent points. The derivatives of these smoothed heating transients were generated using a differentiate/smooth procedure in which a 30 data point Savitsky-Golay smoothing was incorporated. Each heating profile represents the average of ten consecutive heating pulses, which are applied at 10 Hz to the heater. For bare platinum heaters, we observe no appreciable change in heating profile with consecutive application of voltage. The times, temperature, and instantaneous heating rates at the inflection points are shown in Table 1. The uncertainty in assigning nucleation time is the dominant contributor to the uncertainties in nucleation temperature and instantaneous heating rate shown in Table 1. While the absolute uncertainty in nucleation time goes down with increasing heating rate, it is propagated into larger uncertainties in nucleation temperature and instantaneous heating rate.

The observed increase in nucleation temperature with heating rate is consistent with previous studies by Avedisian and Glod, who both explored the relationship

between heating rate and nucleation temperature of water using the method described here.^{1,3} Although the heaters and heating rates employed in these two studies differ significantly from one another, in both studies, nucleation temperature was observed to increase with increased heating rate, ultimately approaching the temperature at which homogeneous nucleation is theoretically predicted to occur.^{8,16} In the study performed by Avedisian et al. on ink-jet printer heads made of a proprietary Ta-Al alloy, the maximum nucleation temperature observed was 282.6 °C at a heating rate of $2.5 \times 10^8 \text{ }^\circ\text{C s}^{-1}$. Glod and coworkers observed the maximum nucleation temperature at the surface of a platinum wire to be 302 °C for heating rates greater than $6.2 \times 10^7 \text{ }^\circ\text{C s}^{-1}$. Our results presented in Figure 5 compare favorably. Here we observe a maximum nucleation temperature of 296 °C at the highest heating rate of $1.09 \times 10^8 \text{ }^\circ\text{C s}^{-1}$.

Study of Monolayer Covered Surfaces

Figure 6 compares heating profiles obtained from a “bare” gold plated heater and the same heater modified with either a hydrophilic [$\text{HO}(\text{CH}_2)_{11}\text{SH}$] or a hydrophobic SAM [$\text{CH}_3(\text{CH}_2)_{11}\text{SH}$]. In this figure, the heating profiles obtained from the SAM coated heaters are the first temperature-time transients recorded after immersion in water. The time, temperature, and instantaneous heating rate at the inflection points are 1.65 μs , 200 °C, $5.8 \times 10^7 \text{ }^\circ\text{C s}^{-1}$; 3.49 μs , 270 °C, $1.44 \times 10^7 \text{ }^\circ\text{C s}^{-1}$; and 3.49 μs , 274 °C, $1.88 \times 10^7 \text{ }^\circ\text{C s}^{-1}$ for the $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ coated, $\text{HO}(\text{CH}_2)_{11}\text{SH}$ coated, and “bare” heaters, respectively. The heater used in the work presented here is driven with approximately the same input power as the platinum heater to which 6 V was applied (see Figure 6), and it should be noted that the heating rate at the inflection point for the “bare” gold heater is very close to

that for the platinum heater at 6 V applied voltage ($1.88 \times 10^7 \text{ }^\circ\text{C s}^{-1}$). The input power was selected to produce a heating rate that had been shown in the above study on platinum heaters to result in nucleation temperatures close to the theoretically predicted value for homogeneous nucleation (see Discussion) of $\sim 300 \text{ }^\circ\text{C}$. In addition, larger input powers were found to produce higher heating rates, which resulted in less dramatic differences between the heating profiles of hydrophobic and hydrophilic SAM coated heaters.

It is apparent that the heating profiles of the hydrophilic SAM covered and “bare” heaters are qualitatively similar to each other and significantly different from that of the hydrophobic SAM covered heater. Closer inspection of the profiles reveals several noteworthy features. First, the bubble nucleation temperature determined from the hydrophobic SAM modified surface, $200 \text{ }^\circ\text{C}$, is markedly lower than those of hydrophilic SAM, $270 \text{ }^\circ\text{C}$, or the “bare” Au surface, $274 \text{ }^\circ\text{C}$. Second, at times greater than $\approx 1.5 \text{ } \mu\text{s}$, the temperature-time transient of the hydrophobic SAM covered microheater shows a significant positive deviation in temperature relative to that of “bare” Au or the hydrophilic SAM covered surface. In other words, the average temperature of the hydrophobic SAM modified heater is hotter than that of the hydrophilic SAM modified surface or “bare” Au surface when subjected to a voltage pulse. Third, we note that differences in heat transfer characteristics of the three microheaters are only observed in the bubble nucleation or boiling regimes of the heaters. Below $\approx 1.5 \text{ } \mu\text{s}$, the time where nucleation is observed for hydrophobic SAM surface, all the heating profiles essentially superimpose indicating that modification of the heater with hydrophobic or hydrophilic SAMs does not significantly affect heat transfer from the gold heater to the liquid in the

pre-boiling regime.

We also observe changes in the heating profiles of SAM modified gold heaters with increasing number of applied voltage pulses. Figure 7 shows the evolution of heating profiles with number of applied heating pulses for a gold plated heater coated with a hydrophilic SAM of $\text{HO}(\text{CH}_2)_{11}\text{SH}$ (Figure 7a) and a hydrophobic SAM of $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ (Figure 7b). Heating profiles after 0 (i.e., pulse number 1), 300, and 1000 heating pulses are shown. For comparison, a heating profile for the “bare” gold heater is also shown in both Figures 7a and 7b. The heating profiles of the $\text{HO}(\text{CH}_2)_{11}\text{SH}$ modified heater change only slightly during the entire 1000 pulse heating schedule. In contrast, those of the $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ modified heater exhibit dramatic changes with successive heating pulses. The bubble nucleation temperature increases and the positive deviation in heater temperature decreases with number of applied heating pulses such that the profile shape more closely resembles that of “bare” gold after 1000 heating pulses.

Figure 8 shows the evolution of heating profiles with number of applied heating pulses for the same gold heater prepared with various SAM surfaces. As in Figure 7, each graph includes heating profiles after 0, 100, 500 and 1000 heating pulses. The three graphs on the left side of Figure 8 are those acquired for the hydrophilic, hydroxy-terminated SAMs of $\text{HO}(\text{CH}_2)_6\text{SH}$, $\text{HO}(\text{CH}_2)_{11}\text{SH}$, and $\text{HO}(\text{CH}_2)_{16}\text{SH}$. These monolayers are known to exhibit advancing contact angles for water of less than 15° .¹⁷ The three graphs on the right side of Figure 8 are heating profiles acquired from hydrophobic SAMs of the n-alkane-thiols: $\text{CH}_3(\text{CH}_2)_7\text{SH}$, $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, and $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$. A study by Bain and coworkers has determined the advancing contact angle for water on these surfaces to be $\approx 115^\circ$.¹⁸ The central point to be noted from Figure 8 is the qualitative

similarity among heating profiles for SAMs of differing length but similar wetting characteristics. These data indicate that the microboiling behavior is largely determined by the short range wetting interactions at the SAM/water interface. In addition, the heating profiles for hydrophilic SAMs evolve less severely with successive heating pulses than those for their comparably sized hydrophobic counterparts. The heating profiles for all hydrophilic SAMs remain similar to that for bare gold throughout the 1000 pulse heating schedule. On the other hand, the heating profiles for all hydrophobic SAMs exhibit initial heating profiles that differ dramatically from that of “bare” gold, yet evolve with successive heating pulses towards the “bare” gold profile. (See Figure 6.)

Figure 9 is a plot of the evolution of nucleation temperature, nucleation time, and average temperature versus number of heating pulses for $\text{HO}(\text{CH}_2)_6\text{SH}$, $\text{HO}(\text{CH}_2)_{11}\text{SH}$, $\text{HO}(\text{CH}_2)_{16}\text{SH}$, $\text{CH}_3(\text{CH}_2)_7\text{SH}$, $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, and $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ coated heater surfaces. We define the average temperature as the average temperature of the heater during the actual heating process. It is determined by integrating the area under the heating profile and dividing by the duration of the heating pulse. It is evident from Figure 9, that there is a rapid increase in nucleation temperature and time with number of heating pulses for the hydrophobic monolayers. In addition, hydrophobic monolayers exhibit a general decrease in average temperature with number of heating pulses. This decrease becomes less rapid with increasing molecular length. The SAM of $\text{CH}_3(\text{CH}_2)_7\text{SH}$ demonstrates the most rapid decrease in average temperature whereas the SAM of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ demonstrates the least rapid decrease. The general trend for the hydrophilic monolayers is to maintain roughly the same nucleation temperature, nucleation time, and average temperature throughout the 960-pulse heating schedule.

DISCUSSION

In this section we discuss the observed heating profiles of SAM covered heaters in the context of simple surface wetting arguments and established models of bubble nucleation. We specifically address the dramatic difference between heating profiles for hydrophobic vs. hydrophilic surfaces and the evolution of these profiles with number of heating pulses.

Figure 10 is a schematic illustration of vapor bubbles and liquid water in contact with hydrophilic and hydrophobic heater surfaces. The contact angles, θ , shown in Figure 10 are defined as the smallest angles made between the liquid-vapor and liquid-solid interfaces of the respective systems. By definition, hydrophilic surfaces are easily wet by water and exhibit small contact angles whereas hydrophobic surfaces are not easily wet and exhibit large contact angles. The limiting thermal layer is shown as a dashed line parallel to the respective heater surfaces. It is defined as the layer of water adjacent to the heater surface, which is hot enough to support the growth of the vapor-phase bubble. In a transient heating process like the one employed in this experiment, the limiting thermal layer thickness, δ , is not constant, but grows in time. In addition, δ will depend on the heating rate. For a specific terminal or maximum heater temperature, faster heating rates will result in smaller values of δ and conversely, slower heating rates will result in larger δ values.

For purposes of discussion, we consider Figure 10 to be a snapshot of vapor-phase bubble growth on transiently heated surfaces. Let's also assume that the bubbles are truncated spheres and that when the snapshot was taken, the bubbles were growing in

time with increasing limiting thermal layer thickness. It is apparent from this figure that the wetting behavior of the heater surface plays a significant role in the growth of bubbles limited in size by the limiting thermal layer thickness. For a given thermal layer thickness, such bubbles formed on hydrophobic SAM surfaces will have larger solid-vapor interfacial areas than those formed on hydrophilic surfaces. Because heat transfer is in general lower through vapor than liquid, bubble growth at a hydrophobic surface is expected to be accompanied by a greater increase in heater temperature than bubble growth occurring at a hydrophilic surface. In other words, we expect boiling at hydrophobic surfaces to be accompanied by a more dramatic increase in heater temperature than boiling at hydrophilic surfaces. As a consequence, we expect the average temperature of heaters with hydrophobic surfaces to be greater than that of heaters with hydrophilic surfaces. This is apparent in the results shown in Figures 8 and 9c. Figure 8 shows a much more dramatic increase in the rate of heating after nucleation for the initial heating profiles of all hydrophobic SAMs as compared to hydrophilic SAMs. Figure 9c illustrates how this is manifested in the average temperature of the heaters during the heating pulse.

The evolution of heating profiles for hydrophobic and hydrophilic monolayers with number of heating pulses can be rationalized by assuming that heating pulses cause thermal desorption of the SAMs. We speculate that each heating pulse thermally desorbs a small fraction of the monolayer thereby exposing an incremental portion of the underlying bare gold surface. Gold is a hydrophilic surface with a measured contact angle comparable to that of the hydroxy-terminated SAM surfaces studied here.¹⁹ It is, therefore, expected that the repeated heating of a hydroxyl-terminated SAM surface will

be accompanied by a minimal change in surface contact angle, and consequently little change in heating profile. In contrast, the repeated heating of an n-alkanethiol SAM surface is expected to result in a large change in contact angle and a significant change in heating profile. Indeed, this behavior is qualitatively observed in Figures 7 and 8. In addition, it is expected that the heating profiles of the hydrophobic n-alkanethiol SAM surfaces will approach those of “bare” gold and the hydroxy-terminated SAM surfaces as the fraction of exposed gold increases with successive heating pulses. This behavior is also apparent in Figures 7 and 8. It is interesting to note, that while there is no clear correlation between molecular length and the rate at which nucleation temperature and time evolve for hydrophobic SAMs, (see Figures 9a and 9b), the average temperature of n-alkanethiol SAM surfaces approaches that of hydrophilic SAM surfaces more quickly with decreasing chain length of the n-alkanethiol molecule (Figure 9c). This trend is consistent with many studies of SAMs indicating that longer chain n-alkanethiols SAMs are stabilized by greater chain-chain interactions.^{20,21} Therefore, the interpretation that gradual thermal desorption of the n-alkanethiol SAMs is responsible for the decay of average heater temperature with heating pulse number (Figure 9c) is consistent with current accepted notions of SAM thermal stability.

We also comment on the short time scale of the heating experiments and its effect on thermal desorption processes. It has been established that alkanethiols start slowly desorbing from gold surfaces when immersed in water at ~75 °C. The temperatures reached in the present study are indeed much higher, approaching 400 °C. However, one must consider the short time scale of the temperature excursions. The application of 1000 5 μ s pulses translates to a total heating time of only 5 ms. While the thermal

stability of alkanethiol SAMs in high temperature water is not known, the observation of significant, persistent differences between hydrophilic and hydrophobic SAM modified heater surfaces suggests that the application of a single heating pulse results in the thermal desorption of only a small fraction of the SAM.

The simple model discussed above and illustrated in Figure 10 accounts for the effect of surface wetting properties on the growth of bubbles already formed and whose uppermost interface is in contact with the limiting thermal layer. It is consistent with the difference, after nucleation occurs, observed in the heating profiles for hydrophobic and hydrophilic SAMs. However, in order to interpret the nucleation temperatures observed in this study, it is necessary to consider mechanisms of bubble formation as well as bubble growth.

Bubble nucleation at the surface of a heater immersed in a liquid may occur as either homogeneous or heterogeneous nucleation. Both nucleation mechanisms will occur at the liquid-solid interface of the heater. In general, homogeneous nucleation refers to the true formation of vapor nuclei where local density fluctuations of the liquid result in the formation of vapor nuclei of critical size from which vapor bubble growth can occur. In contrast, heterogeneous nucleation describes the growth process of incipient vapor nuclei already present at the solid-liquid interface and does not actually refer to a bubble formation process. These incipient nuclei have been traditionally understood to be the consequence of trapped gas at defects or cavities in solid surfaces. Several recent studies that have explored the structure of water at interfaces may be relevant to the process of bubble nucleation at a heater surface. AFM studies by Tyrrell and Attard have revealed the presence, at room temperature, of spontaneously formed

nanobubbles on smooth hydrophobic surfaces.^{22,23} The formation of nanobubbles has recently been linked to the existence of a low-density phase of water that exists close to hydrophobic surfaces.^{24,25} In neutron reflectivity studies of D₂O/deuterated polystyrene interfaces by Steitz et al., it was concluded that a depleted boundary layer of water existed at the hydrophobic polymer surface.²⁴ The depleted water layer was determined to be 2-5 nm thick with a density 6-12% lower than that of bulk D₂O.

Homogeneous and heterogeneous nucleation are both affected by contact angle.¹¹ Carey shows that, for surfaces with contact angles significantly less than 180°, the temperature at which homogeneous nucleation is expected to occur remains close to 300 °C.¹¹ Our heating rate study of platinum heaters (Platinum has a measured contact angle of $\approx 20^\circ$)¹⁹ revealed a nucleation temperature of 286 °C at a heating rate of 1.87×10^7 °C s⁻¹. The nucleation temperatures we observe at comparable heating rates for hydrophilic SAMs range between 270 °C and 284 °C depending on the identity of the SAM and the number of heating pulses (Figure 8a), and the nucleation temperature we observe for a “bare” gold surface is 274 °C. Although these nucleation temperatures are not definitive evidence of homogeneous nucleation, their values do not exclude homogeneous nucleation as the possible mechanism of bubble formation on these surfaces. The nucleation temperatures observed for the hydrophobic SAM surfaces are much lower than those for hydrophilic SAMs (see Figure 8a), with CH₃(CH₂)₁₅SH exhibiting a low nucleation temperature of 197 °C. The large difference between nucleation temperatures for freshly prepared hydrophobic and hydrophilic SAMs suggests that heterogeneous nucleation is occurring on the hydrophobic SAM surfaces.

If heterogeneous nucleation is occurring at our heater surfaces, two questions

arise: 1) how big are these incipient bubbles, and 2) where do they come from? The first question may be addressed by considering the criteria for thermodynamic equilibrium of a gas phase bubble immersed in liquid. Carey derives the following expression for the equilibrium radius of curvature, r_e , of a spherical, vapor-phase bubble immersed in a liquid of temperature T_l .

$$r_e = 2\sigma / (P_{\text{sat}}(T_l) \exp\{v_l[P_l - P_{\text{sat}}(T_l)]/RT_l\} - P_l) \quad (7)$$

Here, R is the ideal gas constant, σ is the surface tension of the liquid at T_l , $P_{\text{sat}}(T_l)$ is the saturation pressure of the liquid at T_l , P_l is the pressure of the liquid (in our experiment 1 atm.), and v_l is the specific volume of the liquid at T_l . The thermodynamic interpretation of r_e is that it represents an unstable equilibrium, and bubbles with a radius of curvature greater than or equal to r_e will spontaneously grow at T_l . Using equation (7) above, we calculate r_e to be 32.9 nm and 76.4 nm at liquid temperatures of 187 °C and 217 °C, respectively. These temperatures are the approximate minimum nucleation temperatures observed for the hydrophobic SAMs of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ and $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$. Our interpretation of this rough calculation is that if there are in fact incipient bubbles present on the hydrophobic surfaces of our heaters, at least some of the incipient bubbles must have radii of curvature roughly as large as the r_e calculated above.

Concerning the origin of the incipient bubbles, SEM images of the device used in this study reveal no defects or pits above the 100 nm resolution of the instrument that might harbor incipient nuclei. THIS IS all wishy washy. Does reference 22 and 23 see any evidence of defects or pits? If not, then you need only say that our system is

consistent with those observations.

CONCLUSIONS

We demonstrate here that fast transient microboiling events are sensitive to the interfacial structure of water by using alkanethiol SAMs to control the surface wetting properties of microheaters. To our knowledge, this is the first study using surfaces of well-defined chemical functionality to establish an unambiguous correlation between surface wetting properties and microboiling behavior. This is already stated in the introduction and the background. I think three instances of tooting your own horn in a paper is unseemly. From temperature-time profiles, parameters such as the bubble nucleation temperature and average heater temperature are determined and found to depend sensitively on the wetting properties of microheater surfaces. Further studies are required to quantify this sensitivity and to determine if this phenomenon can be used as a reliable probe of surface hydration. In this regard, we are currently carrying out studies of microboiling behavior of mixed SAMs to systematically vary surface wetting properties. We speculate that it may be possible to use fast transient microboiling for chemical or biochemical sensing by detecting surface binding events that result in changes to interfacial water structure. The advantages of microboiling for such applications would be its relative simplicity, fast measurement speed, and the inherent miniaturizability of the technique. Other potential applications of the fast transient microboiling method include the determination of thermophysical properties of liquids, the measurement of dynamic interfacial surface tension, the driving of chemical reactions in superheated fluids, and the probing of wetting properties of nanoscale features. The last application is particularly intriguing because bubble nucleation associated with

nanometer sized heaters may exhibit interesting scaling effects. For example, because it takes proportionally more energy to create bubbles of smaller size, the use of nanoscale heaters may offer a route to amplify differences in interfacial solvation properties. There is always the question of whether or not to give away your ideas for future experiments.

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*Certain commercial instruments are identified to adequately specify the experimental procedure. In no case does such identification imply endorsement by the National Institute of Standards and Technology.

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Table 1
Aspects of heating transients shown in figure 5a for bare platinum heater.

Input Voltage	Nucleation Temperature °C	Nucleation Time μ s	Instantaneous Heating Rate °C s ⁻¹
5.6	278±3	4.8±.3	$1.11 \times 10^7 \pm 7 \times 10^5$
6.0	286±4	3.2±.2	$1.88 \times 10^7 \pm 9 \times 10^5$
6.5	300±5	2.4±.1	$4.2 \times 10^7 \pm 2 \times 10^6$
7.8	296±7	1.03±.07	$1.09 \times 10^8 \pm 5 \times 10^6$

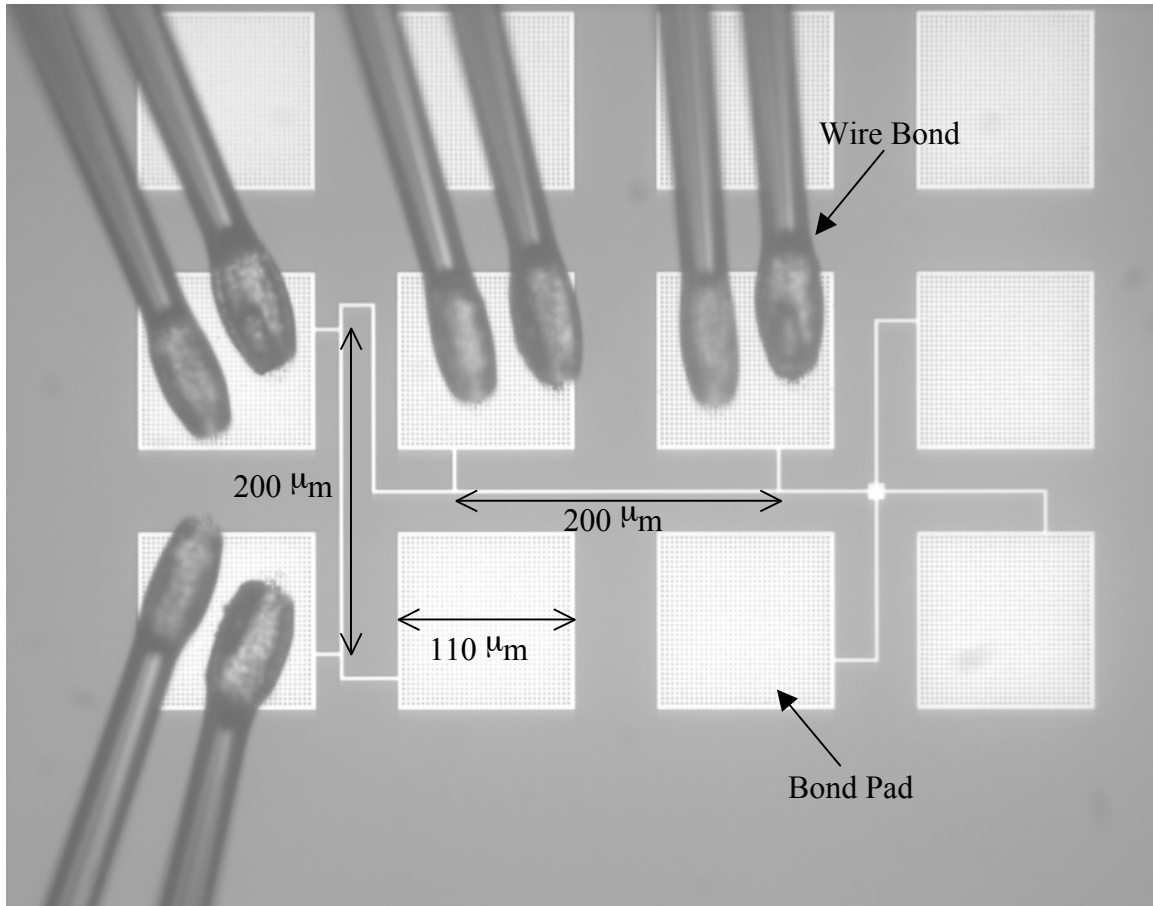


Figure 1. Micrograph of platinum surface heater used in these experiments. Portions of metal trace used as heaters are indicated with arrows and are $\sim 200\ \mu\text{m}$ long.

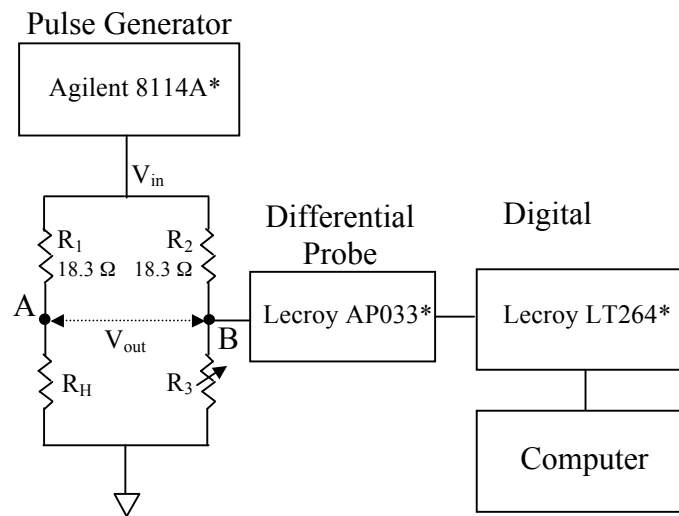


Figure 2. Schematic of experimental setup.

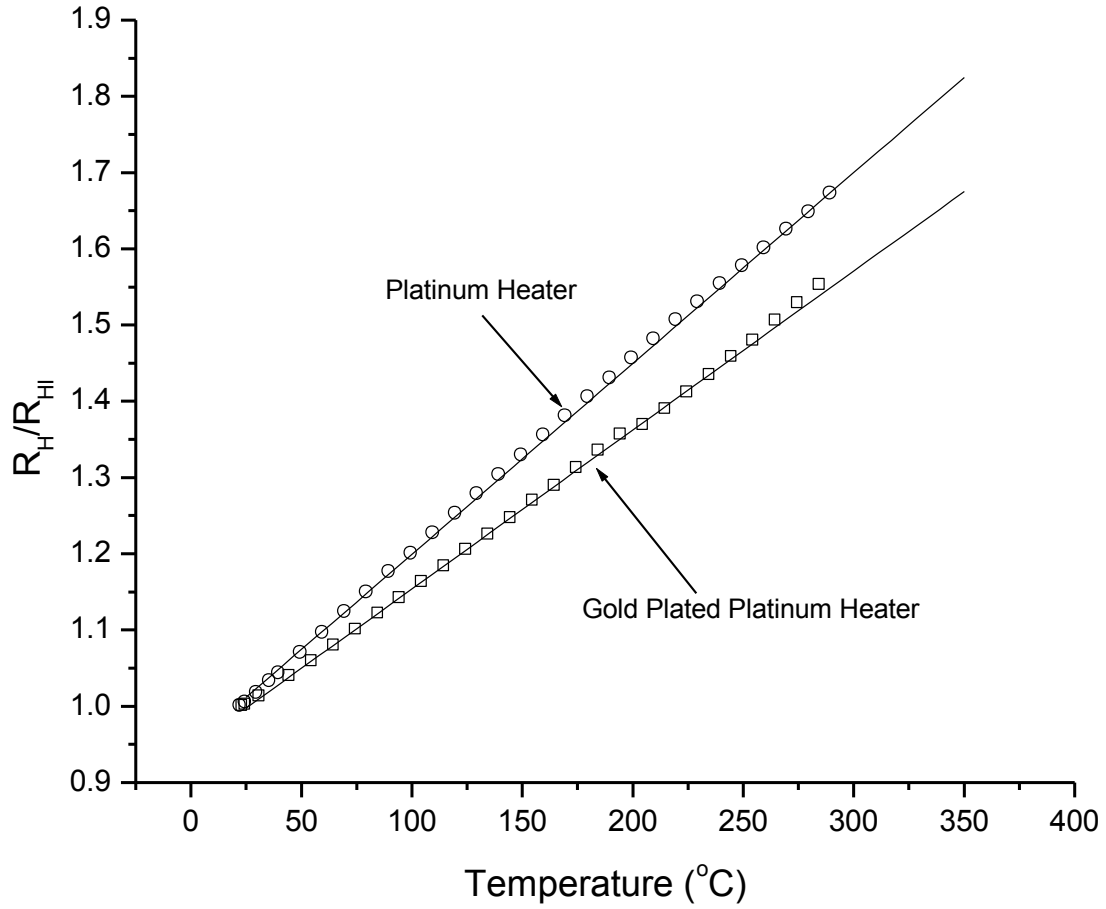


Figure 3. Plot of the ratio of the heater's resistance R_H to its room temperature resistance R_{HI} vs. temperature for both the platinum heater and the gold-plated platinum heater used in this work.

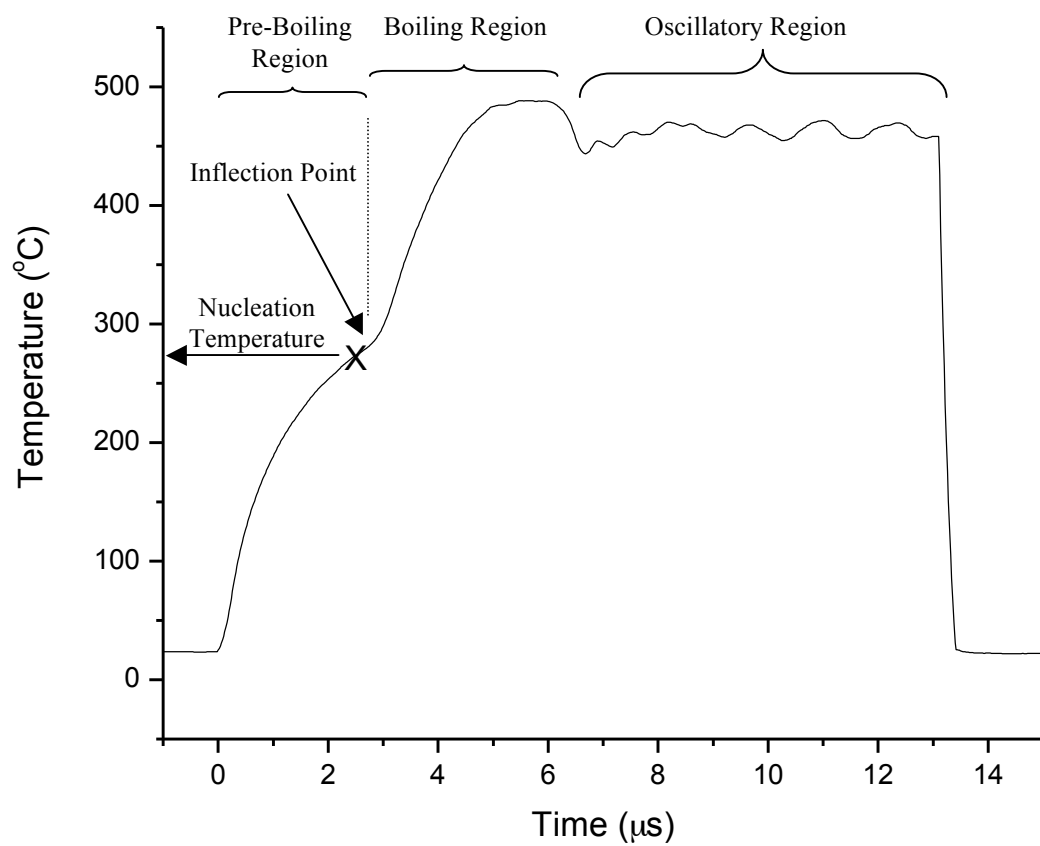


Figure 4. Typical plot of temperature vs. time for a platinum heater, to which a voltage pulse of 6.7 V was applied for 13 μ s.

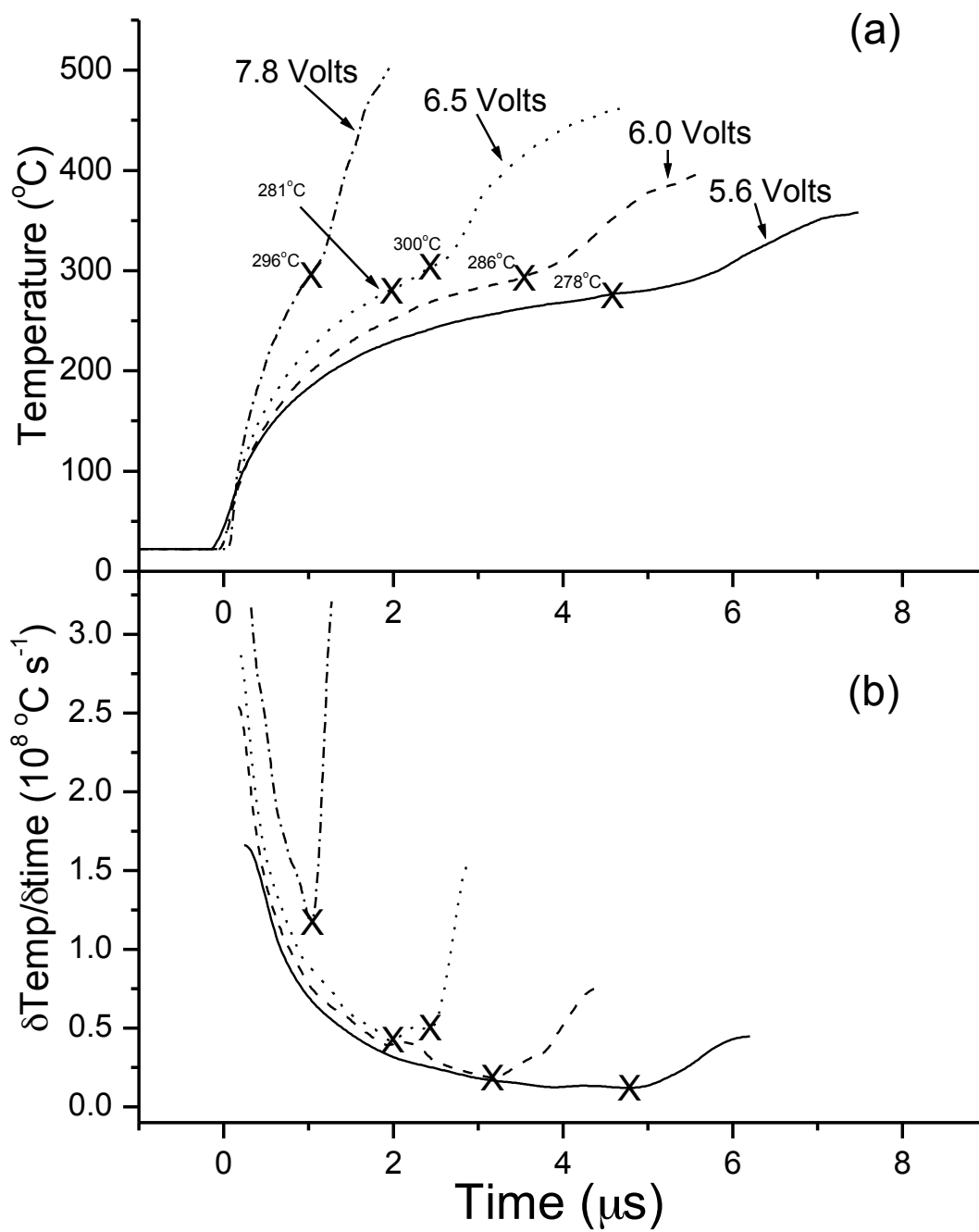


Figure 5. (a) Heating profiles of a platinum heater to which voltage pulses of 5.6, 6.0, 6.5, and 7.8 volts have been applied. (b) First derivatives of these heating profiles. A black “X” on the respective graphs indicates nucleation temperatures. The leftmost “X” on the heating profile and derivative for the 6.5 volt heating pulse indicates a specious inflection point at 281°C, which may be the consequence of a local nucleation event.

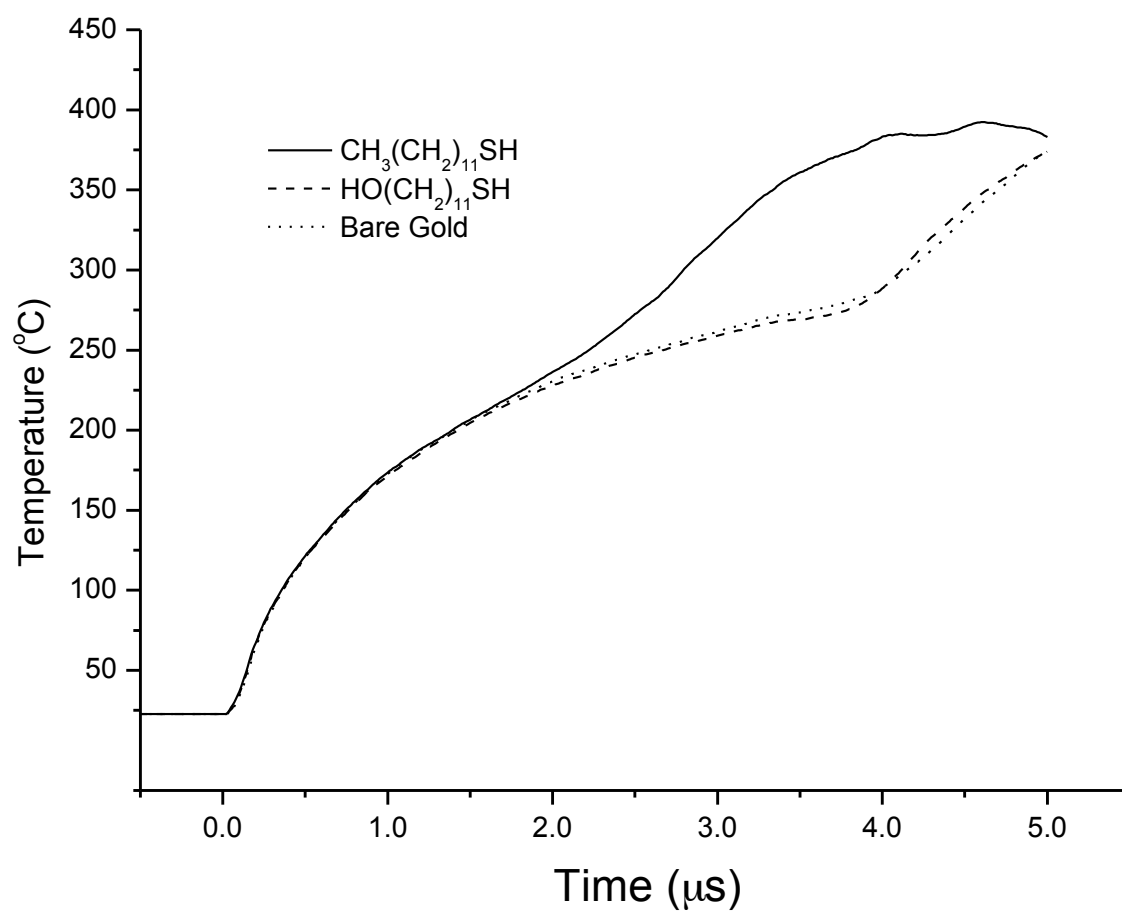


Figure 6. Initial temperature vs. time heating profiles for a bare gold heater, and the same heater coated separately with $\text{HO}(\text{CH}_2)_{11}\text{SH}$ and $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$.

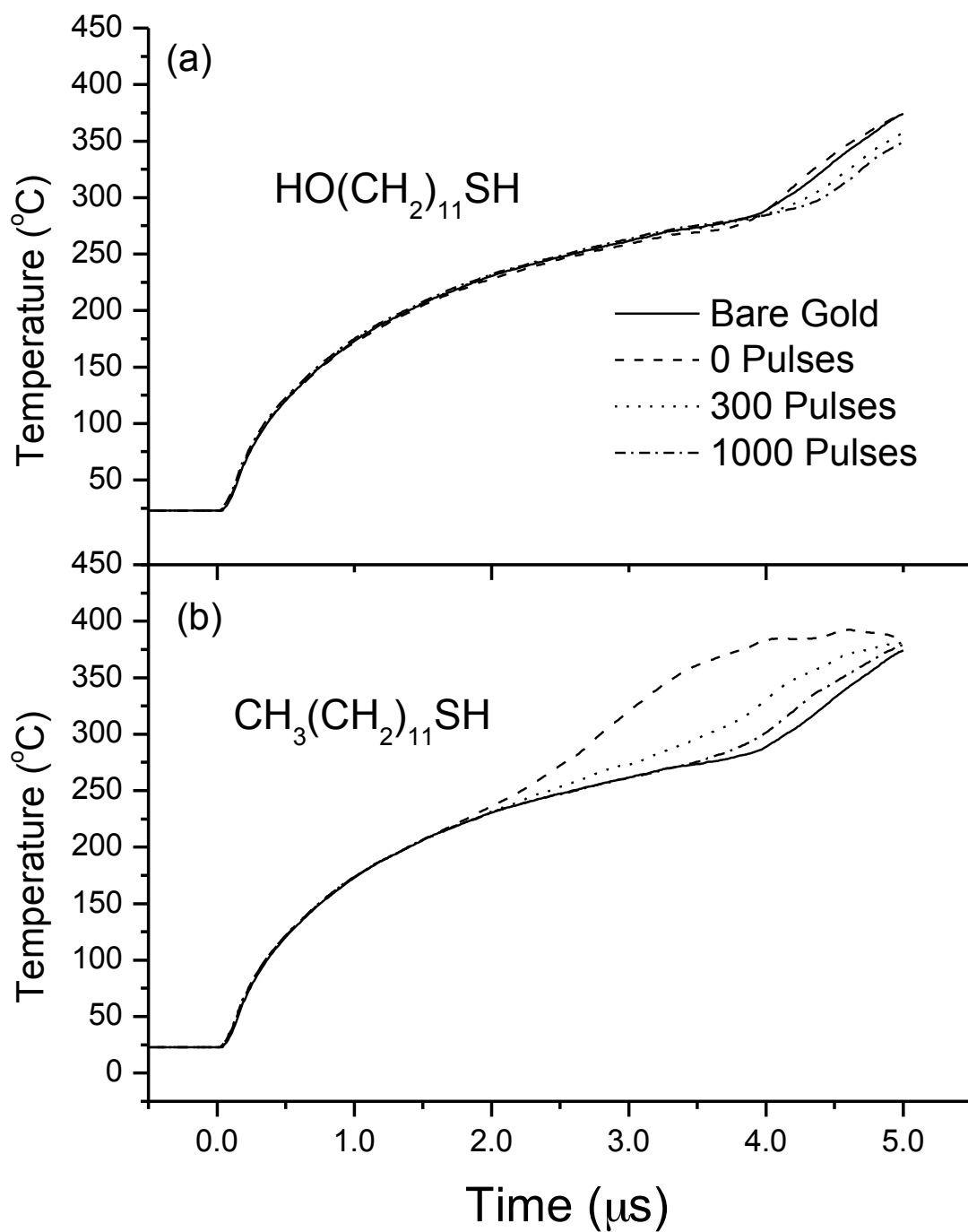


Figure 7. Evolution of temperature vs. time heating profiles with number of heating pulses for a gold plated heater coated with (a) $\text{HO}(\text{CH}_2)_{11}\text{SH}$, and (b) $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$. A temperature vs. time heating profile for the bare gold heater is shown in both frames for comparison.

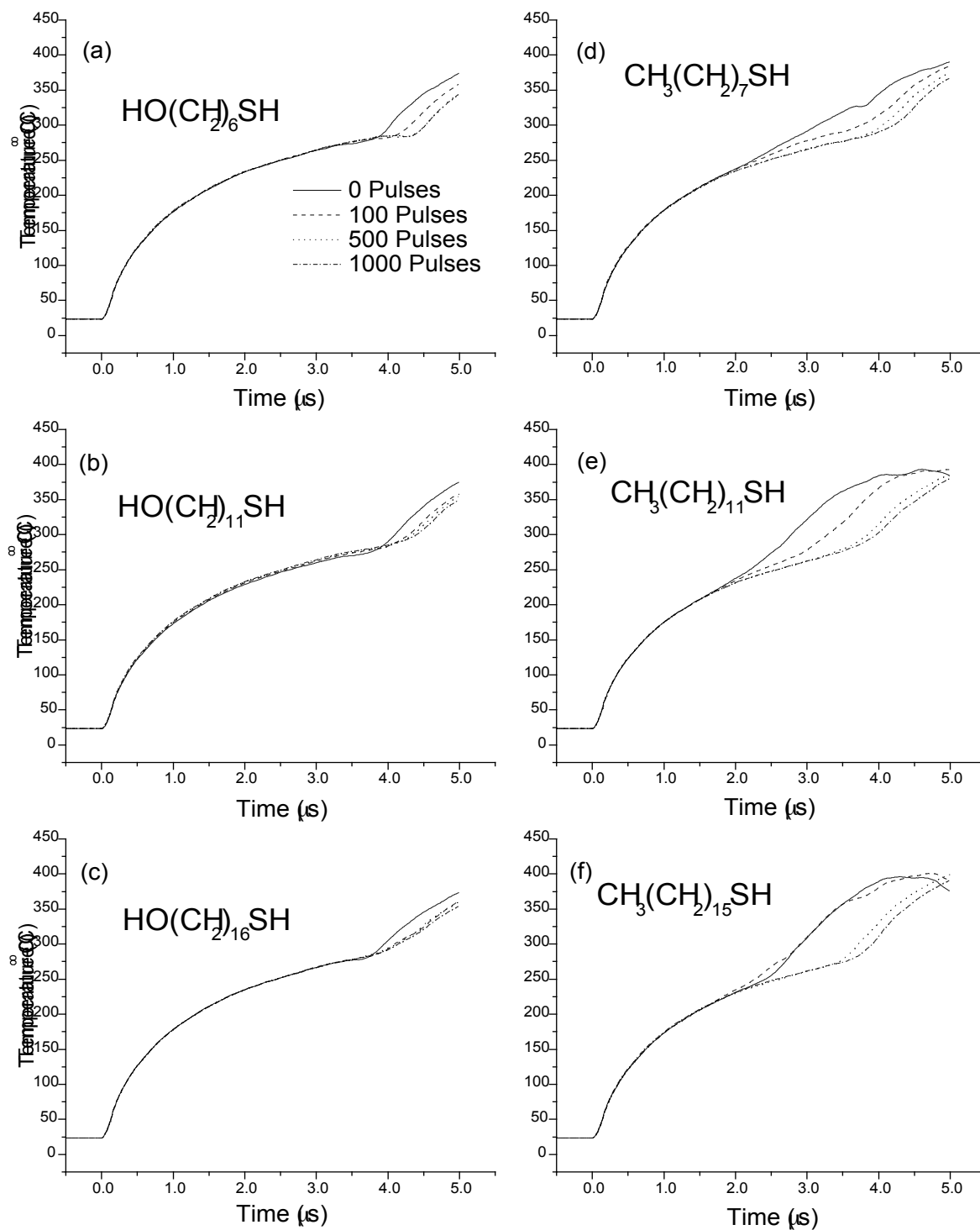


Figure 8. Evolution of temperature vs. time heating profiles with number of heating pulses for a gold plated heater coated with (a) $\text{HO}(\text{CH}_2)_6\text{SH}$, (b) $\text{HO}(\text{CH}_2)_{11}\text{SH}$, (c) $\text{HO}(\text{CH}_2)_{16}\text{SH}$, (d) $\text{CH}_3(\text{CH}_2)_7\text{SH}$, (e) $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, and (f) $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$.

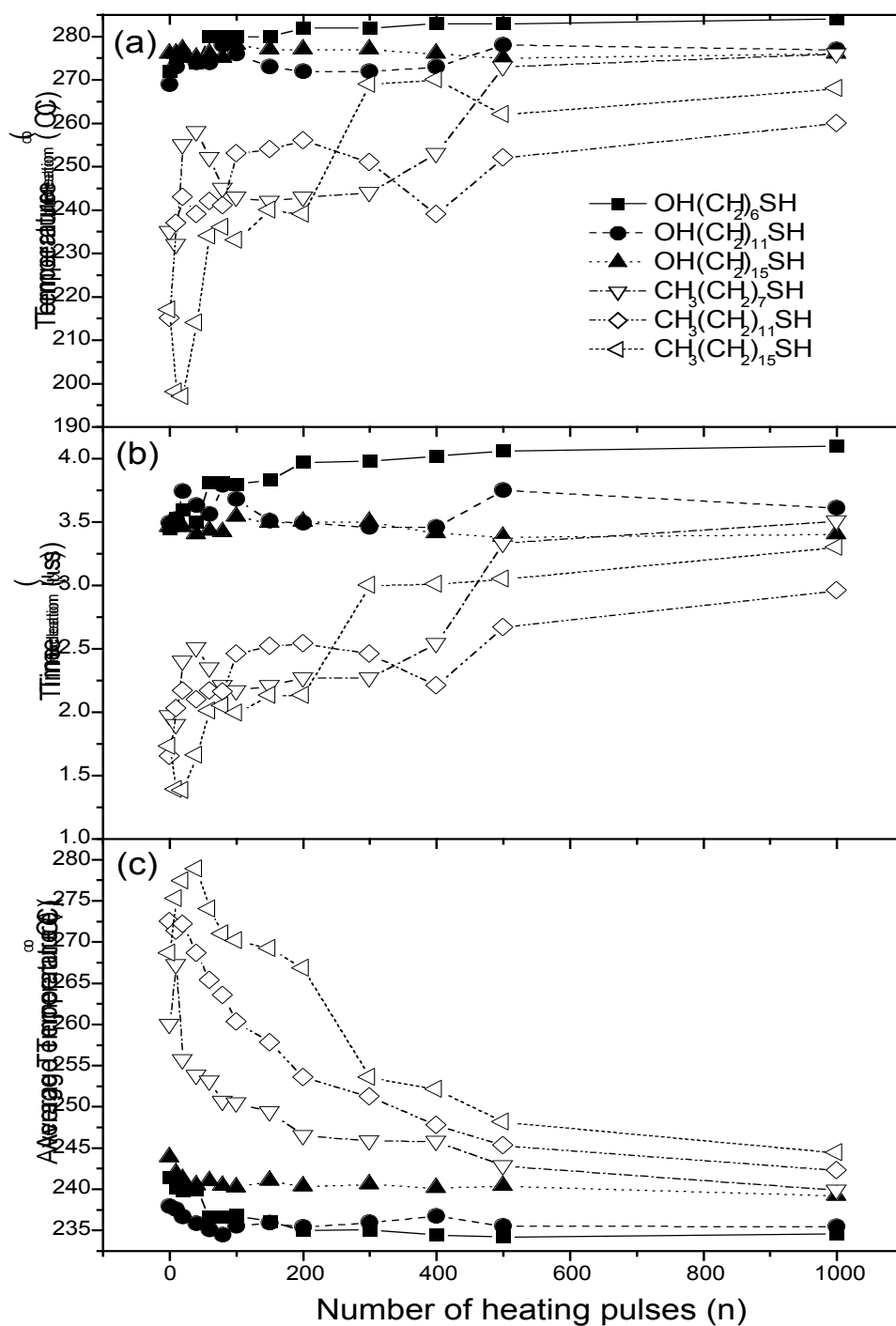


Figure 9. Evolution of (a) nucleation temperature, (b) nucleation time, and (c) average temperature, with number of heating pulses for the heating profiles of a gold plated heater coated with thiols of interest.

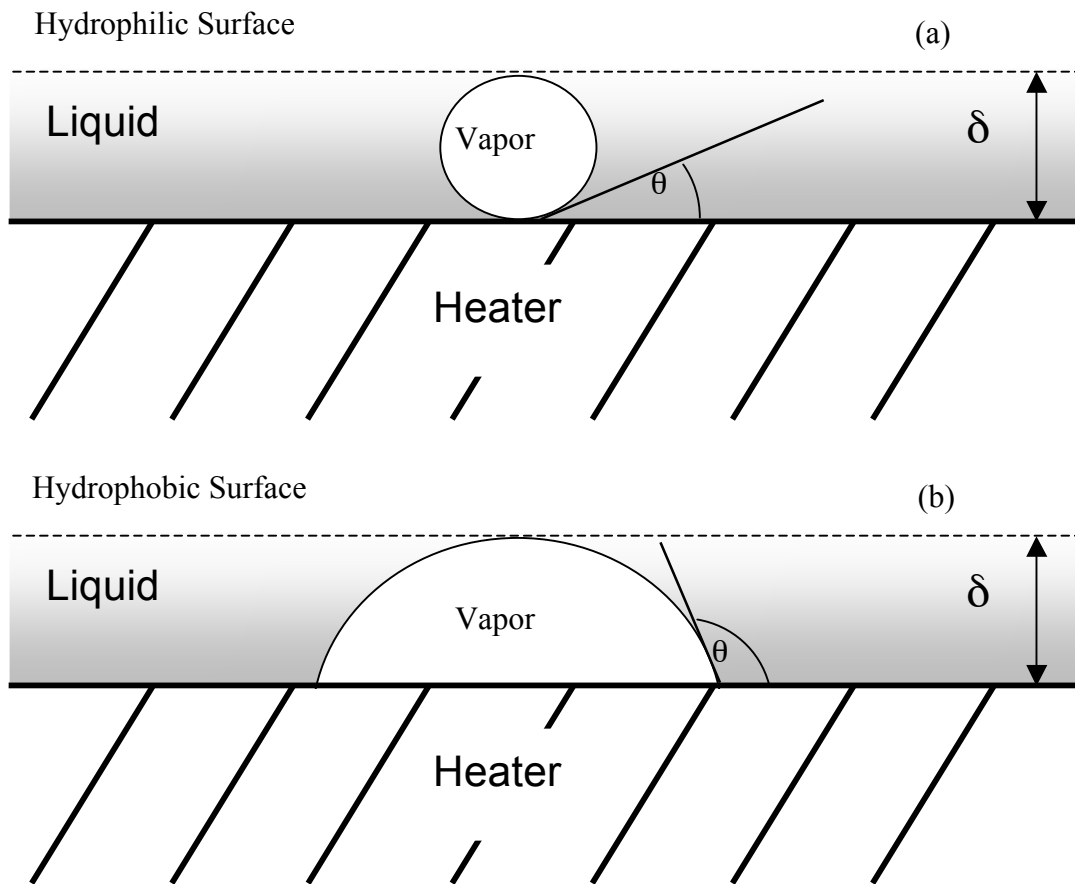


Figure 10. Cartoon of spherical bubble growth on (a) a hydrophilic heater surface and (b) a hydrophobic heater surface. The dashed line tangent to the uppermost surface of the bubbles indicates the top of the limiting thermal layer. The width of this layer is the same in both (a) and (b) and is labeled δ . The contact angles (θ) define the smallest angle made between the liquid-vapor and liquid-heater interfaces.