SIMULTANEOUS NANOTHERMAL ANALYSIS USING HEATED MICROCANTILEVERS

BY

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THESIS

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ABSTRACT

Many important material properties characteristics can be measured using thermal analysis techniques, but macro-systems aren’t ideal for all applications. Conventional systems require large samples, preventing size-dependent studies on thermodynamic properties of a material. Furthermore, some materials cannot be synthesized to the necessary volumes. With the recent advancements in the area of microsensors, nanothermal analysis has improved and gained research interest.

This work presents recent thermal analysis applications performed with a heated microcantilever. Heated microcantilevers have low thermal mass, resulting in high heating rates with quick response times, and are relative isolated to major heat losses, making them well suited for nanothermal analysis. This work discusses the first reported implementation of a microsensor to perform calorimetry and thermogravimetry simultaneously. These techniques were used to investigate thermal dependencies for two studies. The first study discusses nano-thermogravimetry and calorimetry on a 250 pg coal sample. Heat flow and mass change of the sample was measured and used to determine the specific heat capacity. Thermal contact resistance between the heater and the sample was problematic, resulting in uncertainties, and limited the studies investigation into its size-dependent thermal properties. The second study discussed the thermal desorption of mercury from a thin gold film. It was founded that there are two distinct desorption regime that appear to correlate with the unbinding of mono- and multi-layers of mercury. Furthermore, the ambiguous regeneration temperature was found to be 200 °C, regardless of heating rates. This new sensing technique is another tool to help expand the field of nanothermal analysis.
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CHAPTER 1
INTRODUCTION

Microelectromechanical systems (MEMS) sensors are a vital and growing area of research. Their great appeal as a sensor, in general, is due to their small length scale, low cost, high sensitivity, and quick response time. One of first and simplest MEMS devices, and with its adoption to surface topography one of the most common, is the microcantilever. Using conventional laser-based deflection technique, the microcantilevers tip displacement or resonant frequency can be measured. Two different measurement techniques enables it to be a very versatile sensor, allowing the device to be adapted for many different applications. Its sensing capabilities can be categorized into surface and non-surface metrological applications, the latter will be the focus on this work.

In 1994, the first non-surface metrological microcantilevers were reported, measuring humidity changes\(^1\) and heat from a chemical reaction,\(^2\) and since then many improvements have been made to the simple beam in attempts to advance its performance or widen its research applications. One such modification was the integration of an intrinsic resistive heater into its surface. This enabled the cantilever to be used as a heater and a thermometer, opening up the field of nanoscale thermal analysis. The objective of this thesis is to report recent thermal analysis applications performed with a heated microcantilever (HMC). Specifically, the cantilever was adapted to two thermal studies. The first, discuss coal nano-thermogravimetry and calorimetry. The second, will discuss the thermal desorption of mercury from a gold thin film. The motivation behind this research is to contribute in further expanding the field of nanothermal analysis.
CHAPTER 2

BACKGROUND IN HEATED MICROCANTILEVER SENSORS
AND THERMAL ANALYSIS

Understanding a materials properties and behavior is a fundamental principle in material science, and the ability to use and manipulate the material is the core of material engineering. With the technological advancements within the semiconductor industry, introducing more novel approaches to bottom-up fabrication, there is an ever increasing need for understanding and controlling the nanoscale properties of materials. A cornerstone in resolving these properties is performing thermal analysis, and one technique is using a microcantilever as a thermal probe.

2.1 Heated Microcantilever Sensors

MEMS-based thermal analytical measurements are advantageous because of their ability to measure samples down to picograms\textsuperscript{3,4} and nanoliters,\textsuperscript{5} rapid heating and cooling rates exceeding $10^6 \, ^\circ\text{C} / \text{sec,}$\textsuperscript{6-8} and high sensitivity to small temperature changes and heat flows.$^{2,7-10}$ For these reasons, the adaption of integrating a heater into a microcantilever for nanoscale sensing has great appeal. In general, microcantilever-based sensors are quicker and less expensive than equivalent macro-systems, benefiting from reduce size, weight, and power demands (SWaP). Mass sensitive microcantilever resonators, when compared to other microsensors, have a faster response time, lower cost of fabrication, and can operate in gas or liquid environments.\textsuperscript{11}
Heaters have been integrated into microcantilever by selectivity doping the cantilevers surface.\textsuperscript{6} For this work, the cantilevers were fabricated from single-crystal silicon and boron doped using ion implantation. Multistep doping is performed at different concentrations, resulting in two regions of different resistances: a resistive heater (low doped) near its free end, while lower resistive (higher doped) connections were on the cantilever legs. Figure 1 is a scanning electron microscope image of the HMC, indicating the doped regions. Cantilever anchors are used to offset the cantilevers tip, but don’t affect its performance since they are thicker than the rest of the cantilever. The tip is used for topographical application, which is out of the scope of this research. The heater can be electrically addressed for monitoring temperature, via heater resistance, under power control, or for monitoring power under temperature control. The cantilever heater temperature is calibrated using laser Raman spectroscopy, which can be controlled over the range 25-1200 °C \textsuperscript{6,12} with resolution of 5 mK.\textsuperscript{13} Additional microcantilever design, fabrication, and characterization are discussed elsewhere.\textsuperscript{6}

![Figure 1: Heated microcantilever.](image)
A microcantilever sensor may operate under two different modes: static deflection and dynamic resonance. In static mode, deflection due to surface stress acting on the beam or by a point load is measured, whereas in dynamic mode, a change in the cantilever mass is detected by measuring the change in cantilevers resonance frequency. The dynamic mode has been shown to be more sensitive and stable, with respect to vibration and temperature, than static mode, but it also requires more expensive and complicated equipment.\textsuperscript{14} A sub-attogram mass changes and concentrations of 10-100s parts-per-trillion have been detected under dynamic mode.\textsuperscript{15} In addition, it has been observed that cantilevers in dynamic mode perform better with an average higher spring constant of 0.2 N/m, compared with 0.02 N/m under static mode.\textsuperscript{16} This sensitivity relationship can be derived from a simple spring-mass system

\begin{equation}
    m = \frac{k}{4\pi^2 f^2}
\end{equation}

where \( m \) is the cantilevers mass, \( k \) is cantilever spring constant, and \( f \) is its natural resonant frequency. Applying this equation between the initial and final states, sample mass can be calculated.\textsuperscript{17}

The most common technique for detecting cantilever deflection is the optical method using the laser deflection technique, also referred to as an optical lever, and is found in all commercial atomic force microscopes (AFM) for surface metrological applications. The technique reflects a laser off of a cantilever towards a position sensitive photodiode, as shown in Fig. 2. The photodiode is used to determine the laser spot displacement, which is directly proportional to beam displacement. Measuring its resonant frequency requires the addition of a spectrum analyzer, used to convert the time-domain displacements into frequency-domain amplitudes. In modern AFMs, the spectrum analyzer is usually integrated into the AFM controller.
2.2 Thermal Analysis

Thermal analysis is a branch of material science that investigates the temperature dependences of material properties. There are various techniques used to measure these properties, some of which are: calorimetry, thermogravimetry (TG), thermomechanical, thermodilatometry, evolved gas, dynamic mechanical, thermoelectrometry, and thermomagnetometry. Of these, calorimetry and thermogravimetry is the most common types, and will be the focus of both studies.

2.2.1 Calorimetry

Calorimetry is the study of how heat flows through a material with respect to temperature. This has many applications from analytical chemistry in studying heat transfer of chemical reactions, to polymer science, in determining a materials transition temperature. In its simplest form, a calorimetry consists of a heat source and a thermometer, where the power from the source and sample temperature is measured to resolve the calorimetric data. Two common
calorimetry techniques is differential scanning calorimeters (DSC) and differential thermal analysis (DTA). DSC regulates the heater power to maintain a constant temperature between the sample and reference systems. Alternatively, DTA maintains a constant heat flow to the systems while a temperature difference is monitored. These techniques are based on the principle of common mode rejection, where the sample measurement is simultaneously differentiated from a reference measurement, removing environmental and other common signal disturbances. Furthermore, this enables the measurement of the amount of heat flowing into the sample, and not the entire system.

2.2.2 Thermogravimetry

Thermogravimetric analysis (TGA) is the study of how a samples mass changes with respect to temperature. This technique can be used to resolve information regarding to oxidation, moisture content, reaction kinetics,\(^{19}\) and degradation and decomposition temperatures. The method uses a high-precision balance, a heat source, and a thermometer. Unlike calorimetry, differential practices aren’t required since the mass can be directly quantified. Since similar equipment and practices are used for TG and calorimetry, these techniques are often combined and performed concurrently, referred as simultaneous thermal analysis (STA).

2.2.3 Nanoscale Focus

Conventional systems require large samples for analysis, typically > 10 mg, preventing size-dependent studies on thermodynamic properties of a material.\(^{20}\) Alternatively, some materials cannot be synthesized to the necessary volume,\(^{21}\) requiring the use of nanothermal analysis. MEMS-based thermal analytical devices have many advantageous over the conventional systems. Their low thermal mass allows for high heating and cooling rates,
achieving rates greater than $10^6 \text{ K/s}$,\textsuperscript{6-8} with thermal time constants of less than a millisecond\textsuperscript{6} enabling real-time analysis.\textsuperscript{7} These characteristics are essential in resolving rapid thermodynamic phenomena, such that exist in semicrystalline polymers.\textsuperscript{22} These devices can be integrated into a sensor network for addition orthogonal chemical response,\textsuperscript{23} or various forms of spectroscopy.\textsuperscript{20,24} Lastly, resolution sensitivity is improved over conventional systems while using less power and reducing material waste.

MEMS-based microcalorimeters have fabricated into thin-film membranes or bridges,\textsuperscript{5,7,8,23,25} suspended membranes,\textsuperscript{20,26} and cantilevers.\textsuperscript{3,4,9,10,27,28} Both the suspended membrane and cantilever designs are well thermally isolated, but the cantilever design offers the unique advantage of mass detection. With the capability to detect mass, cantilever-based TG devices have also been investigated.\textsuperscript{19,21,29,30} While some studies posed the capabilities of STA\textsuperscript{28} or incorporate larger quartz crystal microbalance devices,\textsuperscript{31} there has been no pervious work of nano-STA MEMS devices.
CHAPTER 3
STA ON SUB-NANOGRAM COAL SAMPLES

Microcantilevers with integrated heaters have been used to perform both calorimetry\textsuperscript{3,28} and thermogravimetry\textsuperscript{19,29,32} on small samples. Calorimetry is possible by measuring both heat flow and temperature of a heater in the microcantilever. TG is performed by measuring the cantilever resonant frequency as a function of cantilever heater temperature. A few studies of gas adsorption\textsuperscript{28,31} have used both gravimetry and heat flow measurements for gas sensing, but no TG was performed. This chapter discusses STA, simultaneous TG calorimetry, using a HMC on a 250 pg coal sample.

3.1 Experiment

Figure 3 shows the experiential setup, which consists of a coal sample placed onto a HMC fixed inside an AFM. Coal samples were loaded onto the 160 \( \mu \text{m} \) long cantilever using the micromanipulator of a wire bonder. Coal was first pulverized into fine size particles and stored in a dry environment. Then, a 25 \( \mu \text{m} \) diameter gold wire was used to transfer the coal to the cantilever tip. The ability to manipulate the coal sample with a single probe is the result of the electrostatic charge of the coal particulates. This charge limited the maximum particle size, since for large samples or high heating rates, the sample would be ejected from the cantilever due to separate charging of the heater during operation.\textsuperscript{33} A compromise between sample lengths of 10-50 \( \mu \text{m} \) and heating rates up to \( 10^2 \, \text{°C/s} \) was sufficient for the present experiments.
Figure 3. (a) Experimental setup of coal on the microcantilever heater-thermometer. The heat flows are shown. The rough side of the coal introduces a thermal contact resistance with the heater. (b) Microscope image of the microcantilever with coal mounted on the heater-thermometer. A micropositioner delivers the coal to the cantilever, and the coal is held in place by electrostatic force.
The cantilever was mounted in an Asylum Research MFP-3D AFM system, adapted for visual inspection of the sample and TG acquisition using laser optical deflection technique. A program was implemented in the AFM controller to continuously measure the cantilever resonant frequency, sampled at 13 sec intervals. Eq. (1) was applied between the initial and final states to determine decomposition mass. The cantilever temperature was increased and both power and temperature were measured through the cantilever electrical properties.

A sample of the recorded voltage and frequency data set is shown Fig. 4. The cantilevers heater power is proportional to the cantilevers voltage; difference between total voltage \( V_{\text{Total}} \) and voltage across a sensing resistor \( V_{\text{Sense}} \). A rapid increase in heater power can be inferred, in Fig. 4.a (and later observed in Fig. 5), from the dip in \( V_{\text{Sense}} \), which stems from the temperature dependent properties of the cantilevers resistance. The calorimetric signal was taken as the difference between the cantilever thermal response in the loaded vs. unloaded state. This common-mode rejection technique removes uncertainties associated with system setup, e.g. heat loss through the cantilever and air. This approach is similar to DTA or DSC in reducing systematic error, but two measurements were made in succession with one device rather than simultaneous measurement between two devices. When required, heating the cantilever to 1100 °C in air could clean the cantilever between experiments.

### 3.2 Heat Transfer Analysis

The heat flow in the system was analyzed using a lumped capacity approach,\(^{34}\) illustrated in Fig. 3(a). Heating power delivered to the sample is limited by conduction through the air and cantilever legs,\(^{20}\) although these power losses can be neglected for the differential measurement.
This heat will result in the sample to undergo decomposition and evaporation. Considerations need to be made into the thermal contact resistance associated with the irregular surface of the coal particles. This will ultimately reduce the power absorbed by the sample $P_s$. Taking account for these heat losses and simplifications, the energy balance on the coal sample can be written as
\[ m \frac{dT}{dt} \left[ c + \frac{dm}{dT} h \right] = P_s \]  

(2)

where \( m \) is sample mass, \( c \) is specific heat capacity, \( h \) is enthalpy, and \( \frac{dT}{dt} \) is the heating rate.

The apparent specific heat capacity \( c^* \) of the sample is attributed by both sensible \((c)\) and latent \( \left( \frac{dm}{dt} h \right) \) heating.

### 3.3 Results and Discussion

Several dozen experiments were performed, with similar data of each set. The following is one of these data sets presented as a single case study. A 250 pg sample with a longitudinal length of 16 µm was placed on a cantilever of spring constant 0.437 N/m, shown in Fig. 5. The voltage was linearly increased from 0 to 50 V in 150 sec, and heater power and temperature were calculated from the measured voltages. Figure 5 shows cantilever power, temperature, and sample mass as a function of time during the heating ramp. The sample underwent three distinct heating regions. In the first two regions, the heating rate was steadily increased to a peak and where it was held at 45 °C/sec between 400-600 °C, after which it dropped to approximately 4 °C/sec for greater temperatures. The transition in heating rates gave rise from the nonlinear thermal properties of the heaters resistance, as the result of linearly ramping \( V_{Total} \). Initial thermal decomposition occurred for temperatures greater than 700 °C, which is higher than its bulk sample measurement, possibly due to high heating rate, thermal contact resistance between the sensor and sample, or small sample size. Around 125 sec, the sample fully decomposed into ash, and at 146 sec (1005 °C), the cantilever mass converges to that of the reference, signifying complete sample decomposition.
Figure 6 shows heat flow extracted from the measured data. For temperatures below 400 °C, endothermic reaction was observed. Moisture was driven out of the sample up to 150-200 °C, which is expected for bulk samples. As the temperature was increased the sample undergoes complex chemical reactions known as devolatilization, where the sample releases and
reacts with volatiles and tars.\textsuperscript{36,37} The series of peaks and valleys of Fig. 6 represent the material phase transitions of softening, melting, and resolidification in bulk sample,\textsuperscript{36} but occurring at lower temperatures. These heating trends have been observed for samples undergoing pyrolysis.\textsuperscript{38}

Figure 6. Heat flow from the microcantilever heater-thermometer, measured as the difference between with the coal mounted and the reference experiment. Coal devolatilization trend is strongly dependent on coal composition.

Figure 7 shows the apparent specific heat capacity and mass loss. A peak heat capacity of 23 MJ/g-K was recorded, which was considerably larger than the bulk measured value of 3 J/g-K. In addition to the devolatilization peak (957 °C), two other peaks form at 620 °C, as the result of the sample softening,\textsuperscript{36} and between 100-200 °C due to the water evaporation. This three peak plot is a characteristic of coal undergoing pyrolysis.\textsuperscript{36} The TG inflection point coincides with the devolatilization peak at 957 °C. The increase in mass at 125 °C may have
occurred due to oxidation, as observed in the bulk sample, but this is unknown since the mass shift lies within one standard deviation of the frequency error. Without knowing the thermal contact resistance, our calculations overestimated the samples true heat flow and heat capacity. Correcting for this heat loss is difficult, as it changes with the sample surface contact area during evaporation, being both spatially and temporal dependent. In addition, rapidly heating the sample seemed to introduce a thermal lag in the system, where only low temperature coal characteristics occur at the appropriate temperature; e.g. water loss. Although difficulties exist in such a system, ridged sample cantilever calorimetry has been successfully performed on n-alkanes.\textsuperscript{4,9,27}

Figure 7. Apparent specific heat capacity and mass decomposition.

Thermal analysis of simple materials can give rise to complex issues when performed using micro-sized samples. These issues are further exacerbated on composite materials, as in
the case of coal. For example the peak heat capacity magnitude and corresponding temperature of coal, in bulk the formation of the peak is from the evolution of methane and hydrocarbons.\textsuperscript{36} From volume estimation, the average thickness of our coal sample is between 1-2 $\mu$m, but reports of pseudohomogeneous maceral units have typical lengths of 2-5 $\mu$m.\textsuperscript{37} It is possible that the pg sample doesn’t have the same composition as in bulk, and therefore other organics are creating the dramatic shift in temperature and peak values. Furthermore, the formation of sample generated atmosphere,\textsuperscript{39} rapid heating rates, and thermal contact resistance may contributed in variation between bulk and pg samples.

The influence of heating rate was further investigated by applying steady state heat pulses. The cantilever was heated by stepping voltage pulses, with widths of one minute, after which TGA was performed using the AFM. Figure 8 displays the TG for samples between 1-5 ng. The long heating pulse ensures that the sample reaches steady state conditions, eliminating shifting of the inflection point from heating rate and sample generated atmosphere conditions. Under these pulse heating conditions, mass shifting on the cantilever became the major measurement source error term, and occasionally adhesive was used to limit movement. The inflection temperature of 710 $^\circ$C measured, indicating a 247 $^\circ$C decreases when compared to the data set in Fig. 7. This difference in heating rates accounts for more than half of the systems calculated thermal lag. Furthermore, when compared to bulk, a difference of 251 $^\circ$C is associated with the size-dependent material properties and thermal contact resistance.
3.4 Summary and Conclusion

In conclusion, this chapter reported simultaneous thermogravimetry calorimeter of a coal sample using a HMC. Calorimetric data was gathered from thermal measurements made with the cantilever heater-thermometer, while the TG data was gathered by monitoring the cantilever resonance during heating. A 250 pg coal sample was deposited onto the cantilevers free-end using a wire-bonder technique, many orders of magnitude smaller than could be measured using a laboratory scale instrument. The uncertainties of the samples surface contact with the heater limited this studies investigation into its size-dependent thermal properties. The sensors MEMS-
based advantageous of high heating rates, high cycle life, and low power, pose the possibilities of rapid characterization of coal.
CHAPTER 4

STA ON MERCURY-GOLD DESORPTION

Exposure to elementary mercury vapor, from fossil fuel emissions, dental amalgam, and even some ritualistic ceremonies, is a serious concern to humans and animals, leading to mercurialism - mercury poisoning. Its bioaccumulation effect poses a greater health risk than acute exposure, creating a need for better long-term environment sensing. A standard approach for mercury detection is based on the principles of gold-mercury amalgamation, which has been implemented into electrical ohmmeter, differential pulse voltammetry, optical reflectivity, various forms of spectrometry, quartz crystal microbalance, surface acoustic wave, and microcantilever resonators.

Recent reports have demonstrated how microcantilevers with integrated heater can be beneficial for self-cleaning or surface regeneration, and applied in the preceding chapter. Understanding the regeneration process requires an investigation into mercury-gold desorption, necessary for mercury dosimeter applications. Pervious mercury-gold thermal desorption studies used discrete measurements to observe general trends, neglecting to investigate the thermal desorption process as a continuum. This chapter investigates the thermal regeneration and desorption process between gold and mercury using a HMC under TGA. Furthermore, calorimetric data is also presented.
4.1 Experiment

The experiential setup and principle of operation is shown in Fig. 9, which consists of a HMC fixed inside an AFM. A thin gold film (100x100x0.23 µm$^3$) was sputtered on the free end of a microcantilever over the 200x100 µm$^2$ heater, the fabrication process is discussed elsewhere. It has a spring constant of 0.756 N/m and resonant frequency of 16.46 kHz. A Teflon enclosure, wrapped with a thin-film heater, was used to position a mercury droplet near the cantilever-gold film. Mercury exposure time was controlled by blocking its cantilever line-of-sight using a cover slip shutter.

The cantilever was loaded by first heating the mercury, Fig. 9.a, which thermally deposited on to the gold film. This resulted in the cantilevers mass to increase, which corresponds to a decrease in resonant frequency. This frequency shift was measured with the laser-deflection technique, using a Digital Instruments AFM head under ambient conditions. The regeneration process, Fig. 9.b, occurs when the cantilever is heated, expelling the mercury.

Figure 9. Experimental setup and principle of operations of the mercury absorption on the gold coated microcantilever. (a) Inside an AFM, mercury was heated and deposited onto the gold. Mercury absorption is indicated by the change of the cantilevers resonant frequency, which was measured using the AFMs laser-deflection setup. (b) Microcantilever heating resulted in desorption of the mercury and regeneration of the gold film. The resistive heater-thermometer and mass measurement allow for TGA.
4.2 Results and Discussion

The dynamic relationship between the cantilevers resonant frequency between its loaded and unloaded states is shown in Fig. 10. Mercury loading on to the HMC is evident by the decrease in frequency with respect to time. The adsorption kinetics is dependent on the mercury-gold interaction, partial pressure, and temperature. Absorption rate increases with an increase in vapor temperature and/or partial pressure. This rate eventually decreased due to limited available unoccupied gold sites for mercury binding. The mercury was unloaded from the cantilever by heating the film. A linear voltage ramp was applied to the integrated heater. At cantilever surface temperature of 100 °C, rapid desorption occurs. The temperature was increased until all the mercury desorbed, occurring near 146 °C. After which the cantilever behaved similar to its unloaded state with increasing temperature. The decrease in resonant frequency of both the regeneration and unloaded signal is due to the cantilevers spring constant temperature dependencies.

There has been a wide range of gold film regeneration temperature reported, varying from temperatures of 150 °C to 200 °C, but desorption has occurred for temperatures at low as 100 °C. It is the authors understanding that these ranges can be contributed to the different desorption temperatures for mercury multi- and mono-layers. Using X-ray photoelectron spectroscopy, Morris et al. reported that multilayer mercury desorption occurs around -33°C and 27°C, and monolayer ranges from 107°C to 144 °C. In Fig. 10, the multilayer desorption can be observed as the shallow slope upon initial heating, and is similar to the absorption kinetics prior to heating. The monolayer desorption can be observed in the rapid frequency change, until it converges with the unloaded cantilever state.
In addition to mercury vapor deposition, bulk condensation deposition was also investigated. The microcantilever was removed from the AFM and placed in a petri dish with mercury, and then heated at an elevated temperature. A relative large frequency change of 500 Hz was measured. Mercury was absorbed by the gold film and condensed on the bare Si and electrodes. TG of the cantilever using both deposition techniques is shown in Fig. 11.a. Different heating rates for the vapor deposition technique were used, and it was observed that slower heating resulted in lower average regeneration temperature of 155 °C. This is a common occurrence in TGA, where longer heating times result in more energy absorption. The change in frequency between the two techniques is comparable; for five and one minute heating times a...
regeneration temperature of approximately 180 °C and 190 °C was determined, respectively. Due to the slight temperature difference, it can be inferred that applying and holding a temperature over 200 °C for a few minutes would complete film regeneration. For bulk condensation, there is a greater frequency shift at lower temperature, as the un-bonded mercury evaporates. Figure 11.b is an optical image of the HMC after surface regeneration. Fluctuations in frequency above 170 °C, ignoring desorption effects, is due to spring constant thermal dependencies and normalization error.

The rate of mercury desorption was also investigated, displayed in Fig. 12. The cantilever was exposed to mercury using the bulk condensation technique. The relationship between the mass desorption rate and cantilever resonant frequency can be calculated by taking the time derivative of Eq. (2), between the measured and final states. At low temperatures, mercury slowly diffuses from the cantilever. Rapid desorption occurs as the temperature increased between 90 °C, corresponding to the first mercury-gold layer breakdown, to 170 °C, and the rate plateaus near 125 °C. This mass rate is a combination of mercury-gold and mercury-silicon desorption. Although the monolayer desorption attenuates near 144 °C, a notable shift in inflection temperature due to heating rates also shifted desorption to 170 °C. From 170 °C to 200 °C, the rate declines as mercury desorbs off of the silicon cantilever, observed in Fig. 11.b. At higher temperatures no additional mercury percolates.

Figure 13 displays the calorimetry information, correlating to the desorption rate data. The mercury-gold desorption is represented by the parabolic heat flow trend, signifying an endothermic process. A minimum heat flow near 110°C was measured, indicating a ‘melting point’ temperature, which closely correlates to its peak desorption acceleration (ng/sec^2). Heat flow stabilizes after desorption.
Figure 11. (a) TGA average trials of the desorption process. Different heating rates were used for the vapor technique, whereas a constant five minute regeneration time was used for the condensation technique (solid black line). (b) Microscope image after film regeneration, for the bulk mercury condensation technique. Remaining mercury droplets can be observed near the cantilevers base and on its substrate. Although the intrinsic heater is only half the cantilever length, high temperature conduction propagated down the cantilever, cleaning it along its length.
4.3 Summary and Conclusion

In conclusion, this chapter reported the regeneration and adsorption process between mercury and a gold film. TGA was performed using a HMC for two loading techniques, which gave comparable results. It was founded that there are two distinct desorption regime that appear to correlate with the unbinding of mono- and multi-layers of mercury. The first regime corresponds to a low temperature shedding of multilayer of mercury, approximately between 27 °C to 90 °C. The second regime corresponds to the higher rate of monolayer desorption of that occurs between 90 °C to 170 °C. Furthermore, desorption occurred for all samples heated above
200 °C, but this temperature decreased to nearly 155 °C for slower regeneration rates, approaching the monolayer desorption temperature.

Figure 13. Calorimetric data from mercury desorption. Decrease in heat flow is the result of endothermic desorption of the mercury from the gold film.
CHAPTER 5
CONCLUSION AND FUTURE WORK

For the first time, a MEMS device has performed simultaneous thermogravimetry and calorimetry; STA. Two STA applications were presented in this work using HMC. HMC are well adapted to thermal analytical measurements, with their low thermal mass resulting in high rates heating and excellent thermal sensitivity.

The first study investigated the thermal properties of sub-nanograms of coal. Heat flow and mass change of the sample was measured and used to determine the specific heat capacity of 250 pg coal sample. Results were compared to bulk measurements performed with a commercial STA system. The uncertainties of the irregular surface contact of the sample with the heater limited the studies investigation into its size-dependent thermal properties. In the second study, mercury-gold film desorption was investigated. Two loading techniques were used, which gave comparable results. It was founded that there are two distinct desorption regime that appear to correlate with the unbinding of mono- and multi-layers of mercury, between 90 °C to 170 °C and 27 °C to 90 °C, respectfully. Finally, film regeneration occurred for all samples, regardless of heating rates, for temperatures above 200 °C.

Future work in nanothermal analysis needs to address the issue of ridged samples. One such a small length scale, thermal contact resistance can dominate the systems response and the magnitude of heat loss. To improve analysis, one approach would be to develop better analytical models to describe heat flow behaviors. Currently nano-STA poses many challenges, but has the potential to assist in new scientific discoveries.
REFERENCES


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