Measuring material softening with nanoscale spatial resolution using heated silicon probes

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Measuring material softening with nanoscale spatial resolution using heated silicon probes

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This article describes the use of heated silicon atomic force microscopy probes to perform local thermal analysis (LTA) of a thin film of polystyrene. The experiments measure film softening behavior with 100 nm spatial resolution, whereas previous research on LTA used probes that had a resolution near 10 μm, which was too large to investigate some types of features. This article demonstrates four methods by which heated silicon probes can perform thermal analysis with nanoscale spatial resolution. The polystyrene softening temperature measured from nanoscale LTA techniques is 120 °C, compared to 100 °C, measured with bulk ellipsometry. The discrepancy is attributed to the thermal contact resistance at the end of the silicon probe tip, on the order of 10^7K/W, which modulates heat flow between the tip and sample and governs the fundamental limits of this technique. The use of a silicon probe for LTA enables bulk fabrication, parallelization for high-throughput analysis, and fabrication of a sharp tip capable of nanoscale spatial resolution.
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I. INTRODUCTION

Many techniques exist for measuring the temperature dependence of material properties. A common technique for measuring chemical and thermodynamic properties is differential scanning calorimetry (DSC). DSC measures phase transitions in a material of interest through observed discontinuities in the material heat capacity. DSC has two drawbacks that limit its application to systems at and below the micron scale. First, DSC measures phase transitions for lumped samples, making DSC insensitive to the variation in phase transition temperature that can occur at surfaces and interfaces in heterogeneous materials. Second, since DSC heats the entire sample mass, it can be destructive and thus not applicable for *in situ* characterization. If the sample is part of a larger system, the system could be compromised as it is heated through the glass transition, melting, or decomposition temperatures of its components. Local thermal analysis (LTA) overcomes these drawbacks by sampling specific regions using a local thermal probe.

A thermally active probe used in atomic force microscopy (AFM) allows the imaging capabilities of AFM to be integrated with local heat delivery for LTA.[1] Figure 1 illustrates the principle of AFM-based LTA, where heat generated by the probe flows through the probe tip into the substrate. In past LTA efforts, the thermally active probe was made from a bent piece of Wollaston wire that formed a Pt/Rh heater tip having a lateral topographic resolution on the order of 1 μm. The probe could generate topographic and thermal contrast images to identify regions of interest using standard AFM imaging techniques and then serve as a localized heat source for thermal analysis.[2,3] Because the substrate was locally heated, the sampled material was confined to the contact region between the hot probe tip and the substrate, allowing specific micron scale heterogeneities, interphase regions, and surface phases to be probed while leaving the remainder of the bulk unperturbed.

LTA has been used in a variety of applications, with lateral sampling resolution typically in the range of tens of microns.[4] One study used LTA to investigate the effects of confinement on thin polymer films by measuring the glass transition temperature (T_g) of polystyrene (PS) thin films as a function of film thickness.[5] Mapping the microscale spatial variation of glass transition temperatures in heterogeneous materials using LTA allowed *in situ* characterization of polymer composite interfaces,[6,7] determination of thermal history,[8] and measurement of photooxidation depth.[9] In pharmaceuticals, LTA determined drug polymorphs on the surface of pharmaceutical tablets *in situ*, which was significant because the surface morphology of active chemicals can play a key role in dissolution within the body.[10] Several studies have compared LTA to conventional DSC and have shown good agreement.[11–13]

Although LTA using the Wollaston probe was effective for measuring phase transitions, the resulting melted crater was not smaller than 1 μm by 500 nm for 100 nm thick polymer films,[5] and exhibited a width on the order of tens of microns for bulk samples.[10] At this resolution, investigating near-surface effects and composite interphase regions, for which the region of interest may be on the order of 100 nm,[9,10,14] is not possible. The resolution limits of the Wollaston probe also prevent examination of three-dimensional nanoscale confinement effects on phase transition temperatures which typically occur below 50 nm for crystalline materials.[15,16] It is therefore desirable to perform thermal analysis with probes having tips sharp enough to achieve nanoscale spatial resolution. Additionally, high-throughput screening can be achieved by performing LTA

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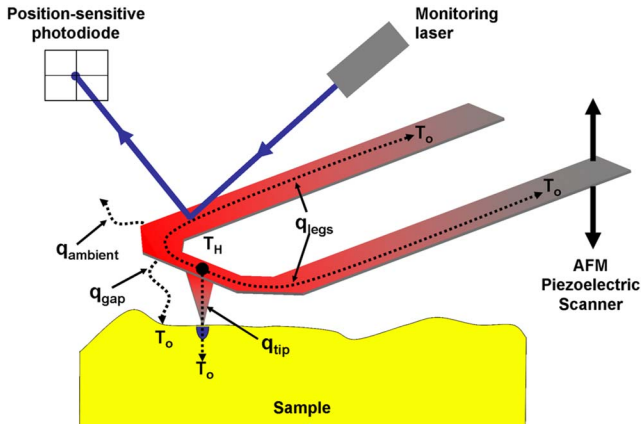

FIG. 1. (Color online) Principle of local thermal analysis. A heated probe is in contact with the sample to be characterized. Heat is generated at the bridge of the probe, marked by the hot temperature T_H, and flows down the legs of the probe, across the air gap, into the ambient environment, and through the tip to the ambient temperature T_o. Phase transitions in the sample cause the tip to sink into the softened sample and change the thermal resistance between the probe and sample. The onset of phase transition can be detected electronically due to the coupling between the thermal and electrical properties of the probe or optically by using a reflected laser to monitor the vertical position of the probe.

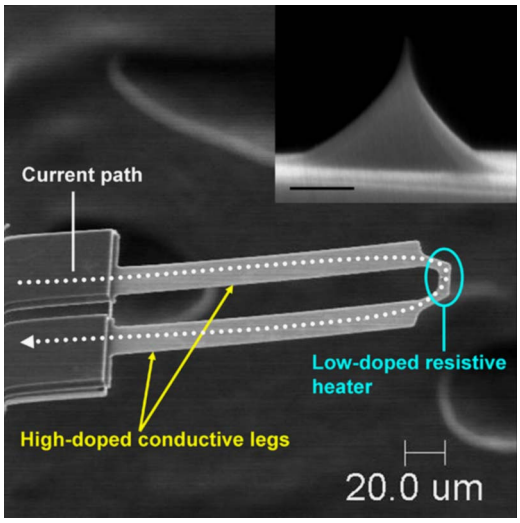

FIG. 2. (Color online) SEM image of microfabricated heated silicon probes. Current to heat the probe flows through the highly doped electrically conductive legs and the low-doped resistive heater at the end. Joule heating in the resistive region results in a temperature rise at the end, which includes the AFM tip. The inset shows a tip with radius of curvature near 20 nm. The scale bar in the inset corresponds to 300 nm.

with multiple probes operating in parallel, which is not practical with the individually fabricated Wollaston probes.[17] The present article describes nanoscale thermal analysis (nano-TA) using batch-fabricated silicon probes with integrated heaters and oxide-sharpened tips with radius of curvature less than 20 nm. The technique can achieve a spatial resolution of about 100 nm.

II. INSTRUMENTATION

The silicon probes described in this article were fabricated by our group using a standard silicon-on-insulator process and are similar to heated probes originally designed for data storage.[18–20] Figure 2 shows one of these probes, which consist of a U-shaped single crystal silicon cantilever, where the legs of the "U" are highly doped and electrically conductive and the bridge of the U is low doped, creating a resistive heater within the current path. When current flows through the probe, resistive heating near the cantilever tip can raise the cantilever tip temperature to over 1000 °C. The silicon probe is batch fabricated, which enables parallelization,[21] low cost, and tip sharpness equivalent to the current state of the art by utilizing oxide sharpening. The radius of curvature at the end of the tip was routinely less than 20 nm. The probes had a tip height of ~1 μm, resonant frequency of 50–150 kHz, and spring constant near 1 N/m, which were calibrated using the thermal noise method.[22] The electrical resistance of the probes was temperature dependent, varying from ~500 Ω at room temperature to ~1 kΩ at ~850 °C, which allowed using the resistance to determine the temperature of the probe. The probe heater temperature T_H was calibrated by using Raman spectroscopy to measure the temperature-dependent shift in the Stokes peak in the Raman spectrum of the heater.[23] Unlike Wollaston probes, organic crystal melting standards could not be used for calibrating the sharper silicon probes due to nanoscale confinement effects on the melting temperature of the crystals.[5,16]

The silicon probes can sensitively measure surface topography through the thermal coupling of the probe to the substrate, eliminating the need for optical instrumentation. The thermal topography measurements are enabled by the topography dependence of the thermal impedance from the probe. As the heated probe scans in contact with a substrate, variations in the surface topography correspond to variation in the thermal impedance between the probe and the substrate.[24–26] The thermal impedance changes can be sensed through the temperature and power signals from the cantilever. Because topography can be measured from the electrical resistance signal of the integrated heater, a laser is not required to measure sample topography or probe deflection. It would be difficult to operate a large array of probes if each probe in the array required a laser-based deflection measurement to measure surface topography. Thus the thermal topography reading critically enables large scale parallelization.

In order to detect phase transitions, LTA requires either the probe displacement to be monitored as it penetrates into a softened substrate, or the simultaneous measurement of temperature and power in order to detect changes to the thermal impedance between the probe and its environment. As a sample undergoes a phase transition, there is a change in the amount of energy required to raise the sample temperature. LTA measures this through changes to the thermal contact between the probe and the substrate.[5,13] When a small amplitude temperature oscillation is superimposed onto the normal LTA temperature ramp, changes to the thermal contact yield similar discontinuities in ac measurements of thermal impedance.[3]

The instrumentation developed for LTA with Wollaston probes is generally not appropriate for performing nano-TA with silicon probes because the heat transfer from the silicon

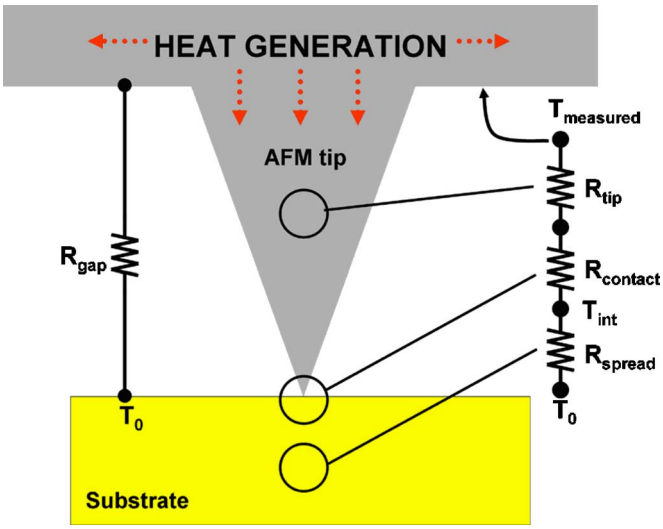

FIG. 3. (Color online) Thermal circuit for heat flow through the tip of a heated AFM probe. The relative sizes of the thermal resistances of the tip (R_{tip}) interface ($R_{contract}$) and substrate (R_{spread}) determine the temperature at the interface between tip and substrate. The dominant mode of heat transfer from probe to substrate is through the air gap, which has a thermal resistance R_{gap}. The calibrated temperature of the probe corresponds to the temperature of the heater region above the tip.

probes is much different than from the Wollaston probes. New instrumentation for nano-TA with a silicon probe should also be compatible with parallel probe operation, since the silicon probe can be parallelized for increased throughput. Optical detection was the most commonly used method to identify substrate softening with Wollaston probes, but it is poorly suited to large scale parallelization. Also, because optical detection measures the physical position of the probe, it can have errors due to the various mechanisms that can cause vertical probe motion in the AFM. Common causes of vertical probe motion include creep of the piezoelectric AFM scanner, thermal expansion of the substrate, and thermal stress-induced bending of the probe.

The sharp tips of the silicon probes constrict heat flow at the end of the tip, making it difficult to determine and control the temperature at the tip-substrate interface, T_{int}. Figure 3 shows the thermal resistance network for heat flow through and around the tip of the silicon probe in contact with a substrate. Due to the sharpness of the tip, the thermal contact resistance ($R_{contact}$) at the end of the tip represents a significant part of the thermal resistance network, which was not the case for the blunter Wollaston probe. The thermal resistance within the tip (R_{tip}) is on the order of 10^6 K/W, and for a polymer substrate $R_{contact}$ and the spreading thermal resistance (R_{spread}) are on the order of 10^7 and 10^8 K/W, respectively. The thermal resistance of the ambient medium (R_{gap}) operates in parallel to R_{tip}, $R_{contact}$, and R_{spread}, and for a given T_H has essentially no effect on T_{int}. R_{tip} can be neglected because it is small compared to $R_{contact}$ and R_{spread}. A significant implication of $R_{contact}$ is that it is large enough to cause T_{int} to be lower than the calibrated T_H.[27]

$R_{contact}$ is sensitive to the contact area between the tip and the substrate, and so T_{int} can depend on the contact force. Precise and repeatable LTA requires the tip-sample contact force to be carefully monitored. In general AFM use, vertical position feedback maintains constant contact force between the tip and substrate. With silicon probes, maintaining constant force is challenging even with feedback because the silicon probes can exhibit thermally induced bending and have temperature-dependent mechanical stiffness.[20] For the silicon probes used here, experiments showed that force was best held constant with vertical position feedback, so feedback was used for all the results shown in this article. In contrast, LTA with Wollaston probes was generally performed without feedback in order to avoid driving the tip into the sample after it softened.[4] This practice minimized the size of the crater left in the substrate and maximized spatial resolution. However, the lack of feedback resulted in a variable contact force due to thermal expansion of the sample and creep in the AFM scanner. Since the Wollaston probe had a negligible $R_{contact}$, the changing contact area had little effect on T_{int}.

Only a small portion of the heat generated in the silicon probe flows through the tip. Figure 1 shows the four heat flow paths from the heater region of the probe: from the heater to the base of the probe through the legs (q_{legs}), from the heater and legs to the substrate through the ambient medium (q_{gap}), from the heater and legs directly to the ambient environment($q_{ambient}$), and from the heater to the substrate through the tip (q_{tip}). About 80% of the power dissipated in the heater flows from the heater to the substrate, of which q_{tip} accounts for only about 0.1%.[27] Changes to the thermal interaction at the tip are thus difficult to detect even though the probe temperature depends upon R_{gap}, which is sensitive to the separation distance between the heater and substrate. In order to stop an experiment at the minimum possible temperature and maximize sampling density, changes to R_{gap} must be detectable at the immediate onset of softening. To capitalize on the potential for nanoscale spatial resolution, new methods of performing thermal analysis must overcome the weak thermal coupling between the silicon probe tip and the substrate.

III. EXPERIMENT AND RESULTS

This section describes four techniques for performing thermal analysis that capitalize on the nanoscale resolution of heated silicon probes and are compatible with parallel operation. For each of the techniques, the sample used was a 44 000 molecular weight PS film of 170 nm thickness spun on a silicon substrate and having a T_g of 100 °C. For each method described, the contact force between the probe tip and the PS substrate was 300 nN. A sourcemeter supplied voltage to the probe and simultaneously measured current. The cantilever was mounted in a commercial AFM system, which provided force feedback, positioning, and topographical imaging.

A. Method 1: Indentation depth

The first method of LTA with silicon probes consisted of holding the probe in contact with the substrate for a specified time, temperature, and contact force, and then moving to new locations and repeating at higher temperatures. After the

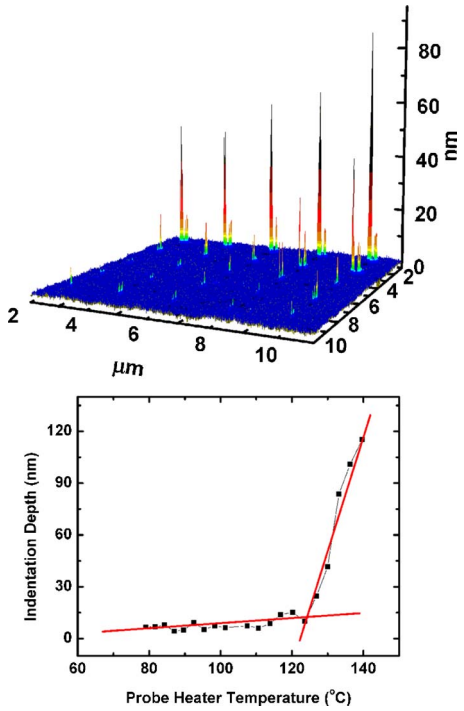

FIG. 4. (Color online) Inverted topography (top) and measured depth (bottom) of indentations made with a heated probe held at various temperatures for 10 s each at 300 nN. Above T_g the indent depth increases rapidly with temperature. The scan size of the topographical image was 10×10 μm^2.

maximum desired temperature was applied, the probe then measured the resultant topography of the substrate. This technique is similar to studies of thresholds for bit formation in thermomechanical data storage[18,28] but differs in two ways. First, in this method, the variation of indentation depth was measured as a function of temperature in order to determine the onset of softening for the substrate. In addition, for thermomechanical data storage the primary concern was determining the threshold for forming data bits in the substrate, whereas in this method the primary concern is characterizing the substrate itself.

Figure 4 shows the inverted topography and the measured penetration depth as a function of T_H for 10 s hold times on the PS film. The temperature was increased from 80 to 140 °C in steps of ~3 °C. Below 120 °C, very little tip penetration into the substrate occurred, whereas above 120 °C the PS substrate was raised above its T_g, increasing the mechanical compliance of the polymer and causing the tip penetration depth to increase roughly linearly with temperature. This method of performing LTA is time intensive, but it yields a clear and reliable transition in compliance behavior and with proper spacing could have a spatial resolution on the order of 1 μm, which is an order of magnitude improvement over the Wollaston probe. Furthermore, since the silicon probes can thermally measure substrate topography, the method is parallelizable.

B. Method 2: Shear modulation to measure tip penetration

Another way to mechanically measure tip penetration into the substrate is through shear modulation.[29,30] In this technique, the tip was stationary while a small in-plane oscillation was applied to the substrate, perpendicular to the legs of the probe. The lateral motion of the substrate applied a frictional force to the end of the probe tip, which exerted a torque on the cantilever and induced lateral motion of the reflected laser on the AFM photodetector. A lock-in amplifier measured the amplitude of the lateral motion of the reflected laser, which was related to the torque on the probe. This technique has been previously demonstrated both with heat supplied to the entire substrate[29] and with locally supplied by the probe,[30] as in this article.

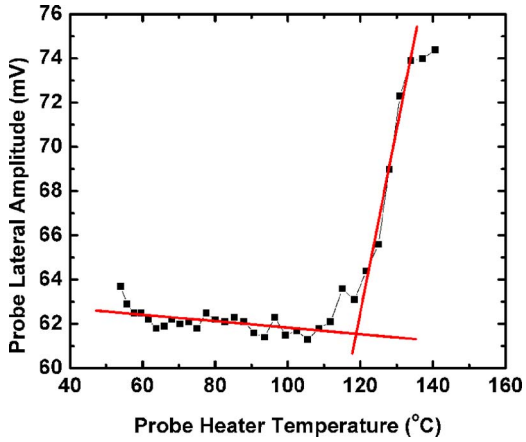

FIG. 5. (Color online) Amplitude of lateral tip motion as a function of probe temperature with the probe tip in contact with a PS substrate that is subjected to 3 nm of lateral oscillation. Above the glass transition, the tip sinks into the PS, which increases the torque on the cantilever and increases the lateral tip motion of the probe.

To demonstrate method 2, the PS substrate was oscillated at 7 kHz with a 3 nm amplitude, while the probe temperature was raised from 50 to 140 °C in increments of ~3 °C. Figure 5 shows the resultant amplitude of the lateral motion of the reflected laser as a function of T_H. A discontinuity in the lateral amplitude occurs near 120 °C due to tip penetration into the softened PS substrate. The torque on the probe increased as the tip penetrated, increasing the torsion experienced by the probe and increasing the lateral motion of the reflected laser. Because of the small lateral motion of the substrate and relatively high contact force, slip at the tip-substrate interface was unlikely to occur.

With this technique, nano-TA is achieved because phase transitions can be sampled in a single sample location rather than over an array of positions as in method 1. The method also gives clear indication of substrate softening without requiring postprocessing, thereby enabling immediate phase transition detection. However, the method requires optical detection of cantilever motion, which is poorly suited to parallelization.

C. Method 3: Differential measurements of thermal impedance

To maintain capability for parallelization, LTA should be performed without using optical detection of cantilever motion. This can be achieved by measuring the probe temperature and dissipated power to monitor changes in dc thermal impedance. By superimposing a small amplitude temperature

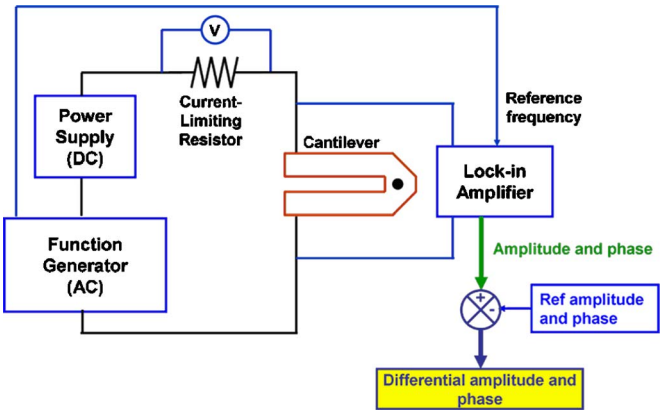

FIG. 6. (Color online) Experimental setup for performing thermal analysis with method 3. A small ac temperature dither is connected in series with a slow temperature ramp. A lock-in amplifier measures the ac phase and amplitude response of the probe, and the reference power, amplitude, and phase are subtracted out numerically.

oscillation onto a slower temperature ramp and measuring the phase and amplitude response of the probe with a lock-in amplifier, ac measurements of thermal impedance can also be made. Figure 6 shows the experimental configuration, which is similar to modulated-temperature DSC (MT-DSC). In MT-DSC, thermodynamic and kinetic information about phase transitions is determined from the difference in total power, thermal phase, and thermal amplitude between the sample of interest and a reference sample, and similar differential measurements can be applied to LTA.

The reference signal used for differential measurements in this method came from recording the power, ac amplitude, and ac phase as a function of T_H with the silicon probe in contact with a glass substrate instead of the polymer sample to be analyzed. The reference data were subtracted from the polymer sample data numerically. This reference signal differs from that used with Wollaston probes, for which the reference signal was taken from a second probe held away from the substrate and subjected to the same temperature ramp as the probe in contact.[3] Using a separate out-of-contact probe for a reference signal neglected the variation in electrical and thermal behaviors between probes and also neglected the differences between the thermal environments in which the probes were placed. Despite these differences in probe characteristics and thermal environment, the differential signals still gave clear indication of substrate phase transitions when used with the Wollaston probe. This reference signal could not be used with silicon probes because the differential signal was dominated by the thermal and electrical differences between probes rather than by changes to the probe-substrate thermal contact.

To demonstrate method 3, the probe temperature was increased from 55 to 135 °C at a rate of ~30 °C/min, while a temperature oscillation was superimposed at a frequency of 20 kHz and amplitude of ~10 °C. Figure 7 shows the total dissipated power and the differential power, ac phase, and ac amplitude as a function of T_H after having subtracted the glass substrate reference data. The differential power exhibited a clear discontinuity at ~120 °C as the PS softened and the tip began to penetrate. The discontinuity was only visible

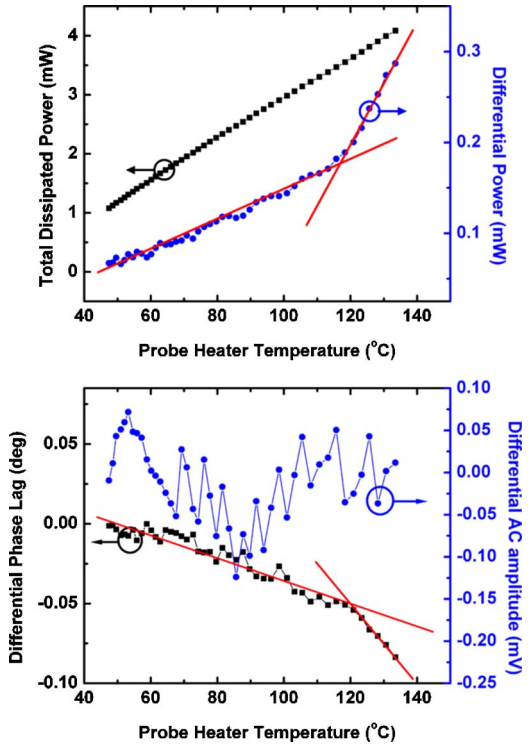

FIG. 7. (Color online) Total and differential dissipated power (top) and differential ac phase and amplitude (bottom) of the probe during a temperature ramp on polystyrene. The differential power exhibits a clear change in slope as the substrate softens, while no transition is visible in the total dissipated power. The differential phase gives a weak indication and the differential amplitude gives no indication of softening. The reference signal for the differential data is taken from a temperature ramp with the probe in contact with a glass substrate.

in the differential signal and could not be seen in the total dissipated power.

The discontinuity in the differential power in Fig. 7 occurred because the thermal impedance between the silicon probe and its environment was proportional to the separation distance between the probe and substrate rather than the thermal properties of the substrate. The total thermal impedance was not sensitive to the thermal properties of the substrate since the thermal impedance of the substrate was small compared to the thermal impedance of the air gap, and so most of the substrate surface beneath the probe was close to ambient temperature. Until the tip began to penetrate into the PS substrate, the separation distance between the probe and substrate was determined by the tip height, causing the reference signals of the probe on a glass substrate to be very close to the signals on the polymer substrate. Once the tip began to penetrate into the substrate and the separation distance between the heater and the substrate started to decrease, the thermal impedance between the probe and substrate became smaller for the softened polymer than for the glass.

In the ac differential measurements of thermal impedance shown in Fig. 7, a slight discontinuity at the softening point of the substrate may have occurred in the phase lag at ~120 °C, but no transition was apparent in the amplitude. With the Wollaston probe, the differential phase and amplitude typically gave clear indication of phase transitions.[3,31] In either case, measuring phase and amplitude adds experi-

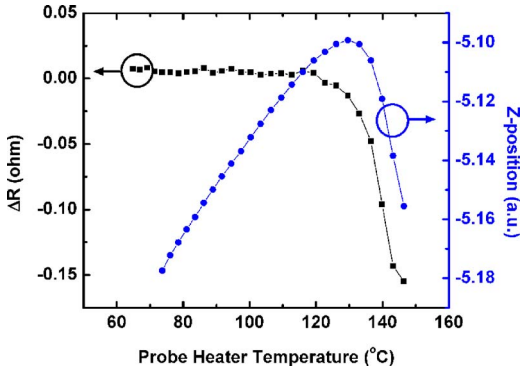

FIG. 8. (Color online) ΔR and deflection as a function of probe temperature while in contact with a PS film using method 4. The optical deflection signal shows significant convolution from vertical deflection mechanisms while ΔR exhibits a clear drop as the tip begins penetrating into the film.

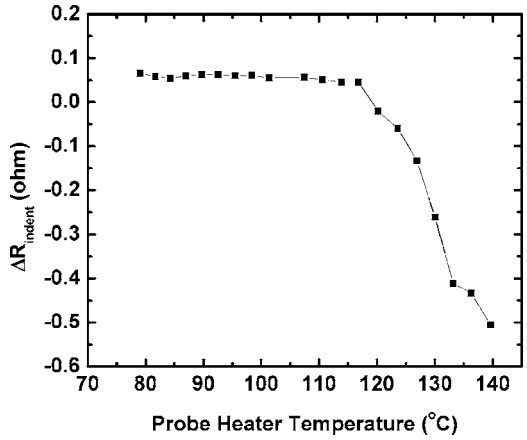

FIG. 9. ΔR_{indent} as a function of indentation temperature for indentations formed using method 1. The data shown were taken during the same experiment as that shown in Fig. 4. Measuring indentation depth from ΔR_{indent} gives a clearer indication of substrate softening than topographical measurement and also eliminates the need for data postprocessing.

mental complexity over simply measuring differential power, yet gives no additional information. Unlike MT-DSC, quantitative thermodynamic and kinetic information cannot be determined from the differential signals because the signals indicate changes in thermal contact rather than changes in the heat capacity of the sample. Differential power, however, does achieve nano-TA with clear phase transition detection but is still not ideal due to the requirement of postprocessing to identify phase transitions.

D. Method 4: Thermally measured tip penetration

To enable immediate phase transition detection with the silicon probes without external optics, methods of performing thermal analysis need to sense variations in the thermal environment of the probe with enough sensitivity to eliminate the need for postprocessing. Immediate phase transition detection was accomplished by performing a stepped temperature ramp and recording the change in probe resistance (ΔR) at each step. The stepped temperature ramp was achieved by stepping the voltage applied to the probe. The experiment increased the probe voltage from 0.8 to 1.38 V in steps of 0.2 V, resulting in a temperature increase from 65 to 145 °C at a rate of ~30 °C/min in steps of ~3 °C. Each voltage was held for 4 s, while the tip was held in continuous contact with the PS substrate.

Figure 8 shows ΔR as a function of T_H for this experiment. At the onset of softening, ΔR changed from a small positive value below the substrate transition temperature to an increasingly negative value above the transition temperature, yielding a sudden decrease in ΔR due to the changing thermal impedance as the tip penetrated into the softened substrate. When the probe was in contact with the PS substrate and T_{int} was below the softening temperature of the PS, the probe temperature and resistance increased slightly with time as the substrate and air gap came into thermal equilibrium with the heater, causing ΔR to be small and positive. When the heater became hot enough to soften the PS, the tip began to penetrate, decreasing the thermal impedance between the probe and the substrate and causing T_H and the probe resistance to decrease, resulting in an increasingly negative value for ΔR. The abrupt drop in ΔR above 120 °C in Fig. 8 was a typical result. Similar results occurred for shorter voltage hold times as well.

Figure 8 shows that measuring ΔR yielded a sharper transition at the softening point of the substrate than optical detection. Because the deflection signal was a measurement of the vertical position of the probe, it was affected by all mechanisms that move the probe vertically. In contrast, ΔR depended only on changes to the thermal impedance between the probe and the substrate, which was primarily determined by the tip penetration, tip height, separation between the legs and the substrate, and tip contact area.

In this implementation of method 4, the change in probe temperature during penetration was small at about 0.35 °C. The sensitivity to changes in thermal impedance could be improved by instead holding either the dissipated power or probe temperature constant at each interval while monitoring either ΔR or the change in power (ΔP), respectively. Whether holding voltage, resistance, or power constant, all three approaches measure changes to the thermal impedance between probe and substrate, but when voltage is held constant, the effect of the changing thermal impedance is divided between ΔR and ΔP. Although more complex than simply stepping the voltage applied to the probe, instrumentation could be used to maintain constant probe temperature or dissipated power.[31–33]

Method 4 can be combined with method 1 to thermally measure tip penetration by measuring ΔR_{indent} as each independent indentation in the indentation array is being formed during method 1. Figure 9 shows ΔR_{indent} as a function of T_H for the array of indentations shown in Fig. 4. The traditionally measured topographical depth is shown as a function of T_H in Fig. 4, and comparing Figs. 4 and 9 shows that indentation depth measured from ΔR_{indent} resulted in less noise and a smoother transition than the topographical depth measurement of method 1. Measuring indentation depth from ΔR_{indent} also eliminated the need for postprocessing, resulting in immediate detection of substrate softening.

Figure 10 shows a typical nano-TA tip crater left behind after a temperature ramp with a silicon probe, outlined by the

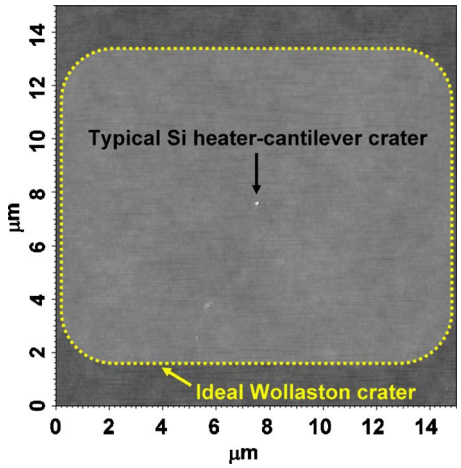

FIG. 10. (Color online) Typical tip crater left behind in the PS substrate by a heated silicon probe after performing a temperature ramp. An ideal crater size for a Wollaston probe is shown for reference and is two orders of magnitude larger in linear dimension.

approximate size of the equivalent LTA crater that would be left by a Wollaston probe. The crater left by the silicon probe is ~200 nm in diameter at its widest point, which is an improvement of two orders of magnitude in sampling resolution and at least four orders of magnitude in sampling volume over the Wollaston probe. The ability to clearly detect softening transitions without external hardware using batch-fabricated probes with nanoscale imaging and sampling resolution may be of use for performing high-throughput, nondestructive LTA.

IV. DISCUSSION

Although the sharp silicon probe tips enable nanoscale spatial resolution, the nanoscale confinement of heat flow also results in difficulties in analyzing experimental results. The polystyrene film had a glass transition temperature of 100 °C, measured by ellipsometry and isothermal uniaxial compression tests, while the measured softening temperatures in Figs. 4, 5, and 7–9 are close to 120 °C. The likely cause of the difference between expected and measured transition temperatures is the thermal contact resistance between the probe and the sample, R_{contact}. The temperatures within the tip-substrate thermal circuit shown in Fig. 3 depend on the relative sizes of R_{contact}, R_{tip}, and R_{spread}, since the resistances are in series with one another. To cause a temperature drop of 20 °C at the interface, R_{contact} would have to be four times smaller than R_{spread}. Assuming diffuse phonon scattering from the crystalline silicon tip into the disordered polymer substrate, R_{contact} is estimated to be $\sim 10^7$ K/W,[27,34] an order of magnitude smaller than R_{spread}, which is on the order of 10^8 K/W. This prediction is lower than the expected 25% to cause a 20 °C temperature drop, but gives close to the right order of magnitude, which is reasonable given the uncertainties inherent to assuming a macroscale R_{spread}, a simplified phonon scattering model,[27] and a Boussinesq contact model.[35] Additionally, just assuming a 17% uncertainty in the spring constant calibration[36] and 10 nm uncertainty in the estimate of the tip radius of curvature can change the ratio of R_{spread} to R_{contact} by a factor of over 4.

The difference between the measured and expected glass transition temperatures could also be due to several other factors. One possibility is a temperature calibration error for the probe. Although temperature calibration errors may contribute in part, the 20 °C temperature difference is larger than would be expected from the 5 °C uncertainty of the Raman spectroscopy technique used in the calibration.[23] Additionally, the measurement of a transition temperature of 20–30 °C higher than the 100 °C bulk transition temperature was verified by several different individually calibrated probes. A calibration error should have a random shift on the apparent transition since the calibration uncertainty is not a systematic bias. However, a more thorough characterization and optimization of the temperature calibration of heated silicon probes is underway and will be presented in a future publication. Another possible cause of the difference between the measured and expected glass transition temperatures is the high hydrostatic pressure beneath the probe tip, which was on the order of 1 GPa. Such a pressure could elevate T_g by over 150 °C.[37] However, such an elevation would cause a T_g much larger than what was measured by the techniques described in this article. Additionally, the variation in the measured T_g for contact forces ranging from 50 to 500 nN was within the experimental uncertainty of the measurement. This can be understood by recognizing that the softening must occur in the PS in areas well outside the contact region of the tip before polymer flow would allow the tip to penetrate. The strains in the material should decay rapidly outside the contact region and thus should exhibit bulk behavior.[29] Confinement effects due to the small thickness of the film are an unlikely cause of the difference between measured and expected transition temperatures because a 170 nm thick PS film should deviate from bulk by less than 1 °C.[5,38]

The offset between T_{int} and T_H could be compensated for when making relative measurements between positions on a sample or between samples with similar thermal conductivities since the effect of R_{contact} should be constant for a given contact force and sample thermal conductivity. However, when comparing LTA on substrates with different thermal resistances or with different contact forces, the degree of offset between T_{int} and T_H can vary. Such variations would make it difficult to measure the spatial variation of phase transitions in the vicinity of composite structures with inhomogeneous thermal properties. In order to understand the accuracy and resolution limits of using silicon probes for thermal analysis, especially in the vicinity of heterogeneities, thermal modeling is necessary to better understand the mechanisms of heat transfer and their sensitivity to substrate properties. Also, although the experiments in this article were performed on flat homogeneous samples, modeling efforts are necessary to help determine the effect of heterogeneous structures and surface topography variation on the accuracy and precision of softening temperature measurements. The modeling can be used to optimize the probe geometry and the ambient medium in which thermal analysis is performed in order to enhance sensitivity to changes in thermal

impedance. Such improved understanding is a necessary step towards expanding the applicability of LTA with silicon probes.

The sampling density of nano-TA can be determined from the size of the melted crater left on the substrate after performing thermal analysis. This size is determined by the shape of the tip, the thickness of the sample being tested, and the heating time. The minimum crater size for the experiments performed in this article was about 125 nm, but distinct indentations have been formed in 40 nm thick polymethyl methacrylate films at a pitch of 40 nm with similar probes.[25] Attaching carbon nanotubes at the end of the tip to increase its aspect ratio could further reduce crater size and increase nano-TA sampling density.[39] Even with a crater size of 125 nm for the probes used in this article, some results of nano-TA performed with the same probe on a granular organic material have suggested that individual grains could be independently sampled, implying that the actual area sampled by the tip may be less than 50×50 nm^2. Besides the PS samples described in this article, nano-TA has also been applied to various organic crystals, and the results have shown a significant depression in melting temperature.[16] Thus, heated silicon probes are also a potential tool for characterizing nanoscale confinement effects on melting temperature in crystalline materials.

This article describes the use of batch-fabricated heated silicon probes to achieve nano-TA. Four parallelizable techniques of performing nano-TA are demonstrated with spatial resolutions between 100 nm and 1 μm, which is one to two orders of magnitude improvement over past techniques. Phase transitions are optimally identified from measuring changes to the thermal impedance between the probe and substrate as the tip penetrates into the softened substrate. The development of parallelizable techniques could be used with probe arrays that have previously been operated with similar probes, which could enable high-throughput analysis.[21] The ability to sample with nanoscale spatial resolution and precision enables using nano-TA for characterization of pharmaceuticals, composites, near-surface phenomena, and nanoscale confinement effects over length scales too small to be analyzed by other techniques. A thermal contact resistance exists between the probe tip and the substrate, necessitating further modeling to characterize the uncertainties pertaining to absolute measurements of transition temperatures.

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