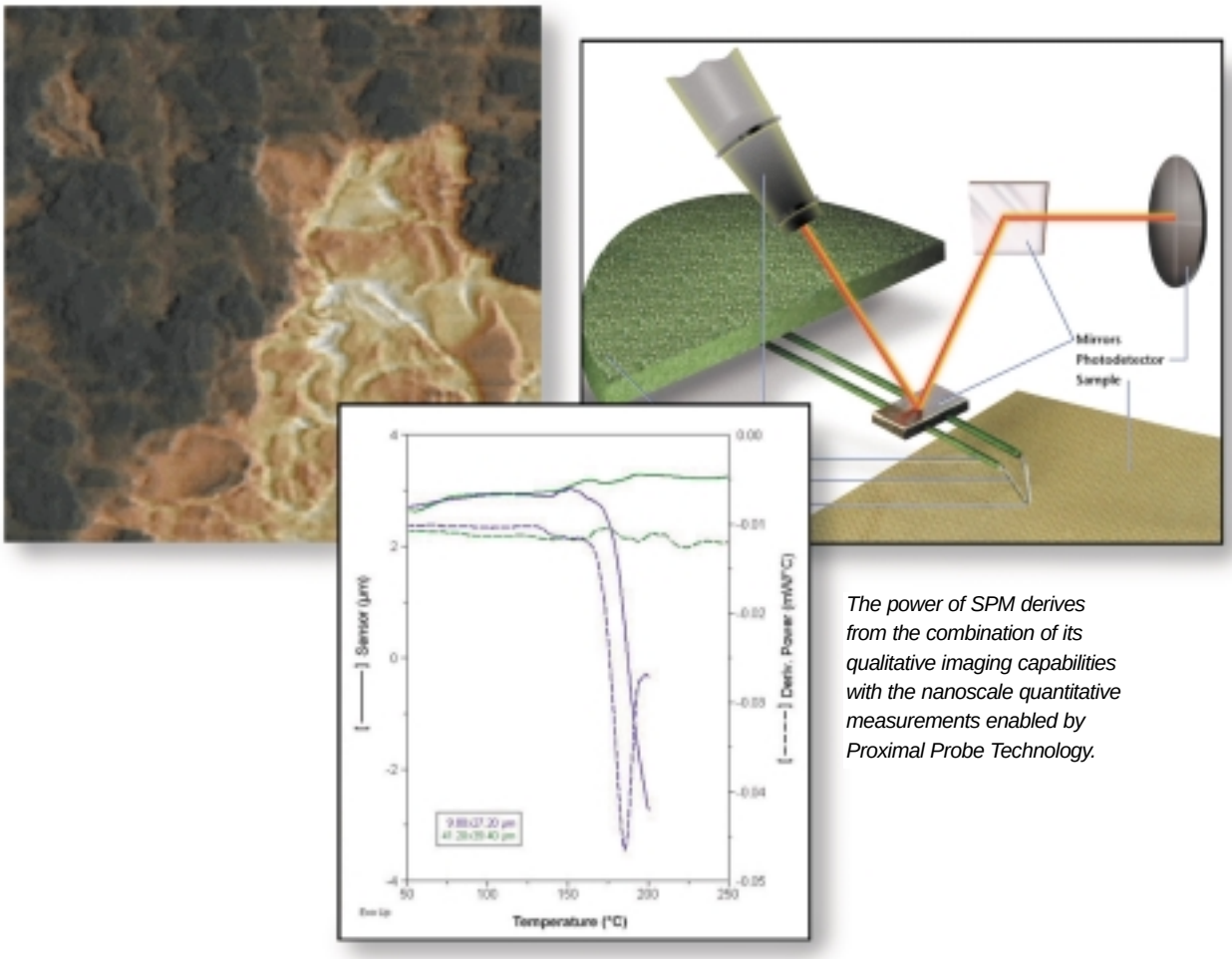
technical report




*The power of SPM derives from the combination of its qualitative imaging capabilities with the nanoscale quantitative measurements enabled by Proximal Probe Technology.*

# *Proximal Probe Technology™*

# *for Scanning Probe Microscopes*

THERMOMICROSCOPES

# Introduction:
# When is a microscope more than a microscope?

Traditionally, the field of microscopy has centered on the creation of highly magnified images of things too small to be seen with the eye alone. This was certainly the case with Scanning Probe Microscopy, which burst onto the scene some 15 years ago with dramatic images of individual atoms. We are visual beings and the rapid acceptance of SPM followed directly from its ability to represent physical interactions in an intuitive image format. However, much of the value of SPM today derives from its ability to detect and measure a wide variety of specific interactions between its scanning probe and the sample. As the technology continues to mature, emphasis is shifting from its ability to display these signals as images to its ability to quantify and measure them. The SPM today is much more than a microscope, it is truly a micro-probe in the fullest sense of the term, providing investigators with a versatile tool that can probe and measure a broad range of specific material properties on the nanometer spatial scale.

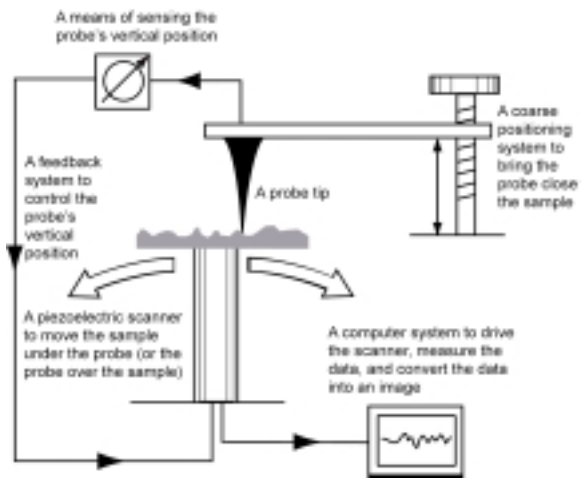
Much of material science today focuses on the properties of and interactions between materials that are segregated in microscopic domains, or between these domains and the environment. Polymer scientists want to measure the physical characteristics (adhesion, compliance, friction) and thermal characteristics (conductivity, expansion, phase transition temperature, calorimetry) of individual components in a blended or composite polymer. Semiconductor engineers need to measure the physical dimensions of the structures they create, as well as electrical properties such as capacitance, conductivity, and potential. Biologists may want to measure the binding forces between a specific biomolecule and its receptor site on a cell surface or between antigens and antibodies, or to observe and localize single molecule fluorescence. The list of potential SPM applications is endless and we will look more closely at several.

What all of these applications have in common is the need to quantify some specific probe/sample interaction. This places demands on the SPM that, in many cases, go far beyond the ability to sense changes in the interaction and map the changes into an image. Recognizing that the greatest value of SPM lies in its measurement capabilities, ThermoMicroscopes has invested heavily in developing the technology required to quantify the interactions between a sample and a probe held in close proximity to it. The result is Proximal Probe Technology (PPT™), an integrated set of technologies unique in the industry that enables ThermoMicroscopes' SPMs to make the most accurate and precise proximity measurements among all commercial available systems. Before exploring these in more detail, let's

## SPM Basics

revisit some SPM basics. All SPMs acquire data by monitoring the behavior a finely tipped probe as it moves through a scanning pattern in contact with or close proximity to the sample surface. Usually the instrument presents the data array as an easily interpreted image that correlates the monitored signal with the sampled location. The probe is attached to a flexible cantilever that deflects in response to forces exerted on the probe by the sample. The mapped signal may be the deflection of the cantilever's free end, the displacement required at its fixed end to maintain constant deflection (force) of the free end, shifts in phase or amplitude as the cantilever oscillates at resonant frequency above the sample surface, or a variety of other signals.

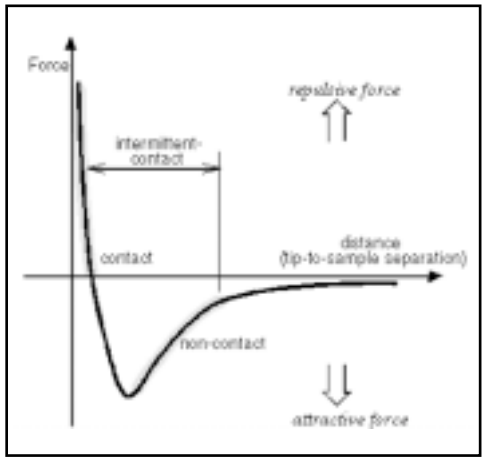
SPMs typically operate in one of several modes, char-




*All SPMs generate an image by scanning a finely tipped probe over the sample surface.*



*Cover image: The image set summarizes the value of PPT: the thermal probe (schematic) is used to generate the thermal conductivity map (image) from which the*




*Different SPM scanning modes can be classified by the forces they monitor and the distance between the tip and the sample surface over which the forces operate.*

acterized by the extent of contact between the probe and the sample. The first SPM, the Scanning Tunneling Microscope (STM), monitored the tunneling current between the probe and the sample. STM is a non-contact mode in which the monitored signal is either the change in tunneling current measured by a constant-height probe, or the change in probe height required to maintain constant tunneling current.

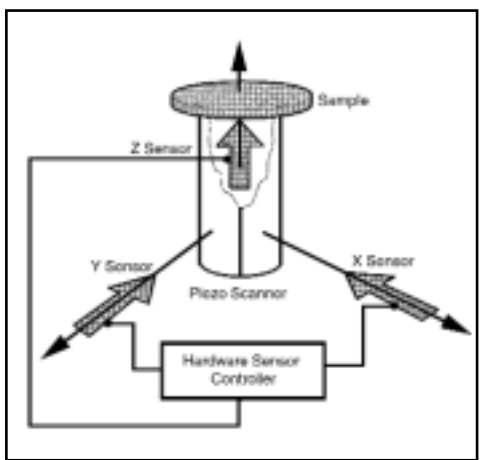
STM was soon followed by Atomic Force Microscopy (AFM). Early AFMs operated in contact mode. The probe remained in constant contact with the sample surface and changes in probe position reflected surface topography.
Certain measurements, such as friction, compliance, adhesion and some thermal characteristics, require contact with the sample; however, contact mode has the potential to introduce measurement artifacts by damaging the probe tip or the sample or both.

Intermittent Contact mode (IC) was developed as a way to reduce the shear forces and concomitant artifacts generated by contact scanning. In IC mode, the probe moves through relatively large oscillations that bring it into periodic contact with the sample. IC mode reduces the damage caused by shear forces in contact mode and often provides good contrast for imaging. However, the dynamics of the collision between the probe and the sample surface are difficult to model quantitatively. Furthermore, although IC mode greatly reduces damage to the sample, the probe still degrades over time, introducing another unknown, and probably unknowable, factor into IC mode quantification.

One of the key components of PPT is the Near Contact™ mode. In this mode the probe oscillates at high frequency and low amplitude in close proximity to the sample surface. The oscillations improve the probe's sensitivity to weak, short-range forces, and increase the accuracy and precision of the measurements. Because there is no contact with the sample, all damage to the probe and the sample is eliminated. Furthermore, the probe's oscillations are not disrupted by contact with the sample surface and yield readily to mechanical analysis, thus providing detailed information about interactions between the probe and the sample.

## Proximal Probe Technology

Proximal Probe Technology is the integrated set of technologies that permit ThermoMicroscopes SPMs to make highly accurate measurements of the interactions between the scanned probe and the sample. Although all SPMs are potentially sensitive to the same interactions, accurate measurements require a number of specific capabilities. These fall roughly into three categories—scanning accuracy, probe design, and probe modulation/signal detection.
All commercially available SPMs use piezoelectric scanners to move the probe relative to the sample. Piezoelectric materials extend or

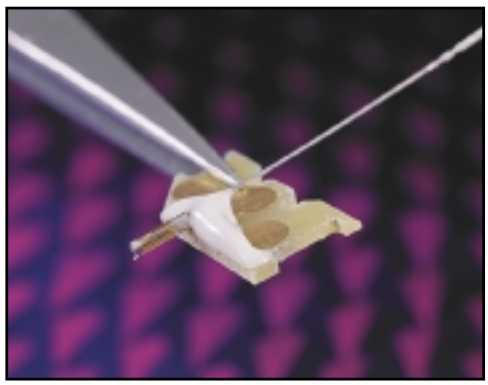


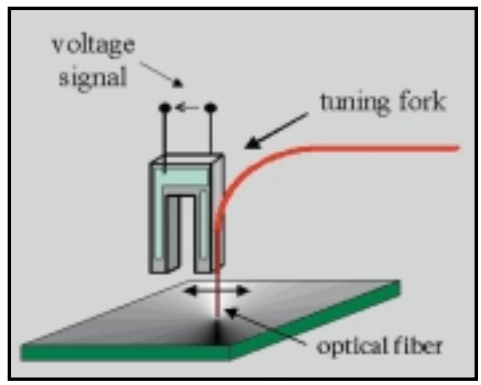

*Real-time scanner position sensing and feedback is essential for accurate scanning.*

**Scan Linearization**

retract in response to an applied electric potential. Although they provide very fine movement control, piezo scanners exhibit several well-known non-linearities in their response. These include hysteresis, creep, and variable historical effects. Some of these errors can be modeled and predictively corrected, others are inherently unpredictable. Accurate control of the probe scan motion requires active position sensing and closed-loop feedback to the scan control system. (See Correcting Scan Errors in Scanning Probe Microscopes, *Microscopy Today*, September, 1999.) All spatial measurements in an SPM presume the accuracy of the scan. Any scanning error contributes directly to measurement error. ThermoMicroscopes provides active closed-loop scan correction on all of its SPMs. The corrections are based on patented optical or capacitance position sensing and provide the fastest, most accurate corrections available.

Many measurements require specifically designed probes capable of eliciting and/or detecting the desired interaction with the sample. Scanning Thermal Microscopy (SThM) and Near-






*Specialized probes are required to measure many material properties. For NSOM, an optical fiber, coated and drawn to a very small aperture, is modulated in close proximity to the surface by an electrically driven tuning*

**Probe Design**

field Scanning Optical Microscopy (NSOM) are two examples. SThM uses a heated probe and measures the electrical current required to maintain it at a constant, elevated temperature as it scans the sample surface. Changes in local thermal conductivity cause fluctuations in the required heating current.

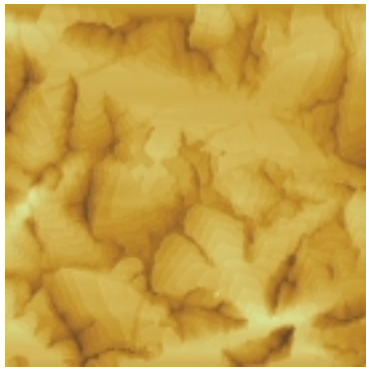
Micro-Thermal Analysis (*µTA*™) uses the same heated probe to derive calorimetric information from a sample volume of a few cubic microns by plotting the amount of heat required to raise the sample temperature. µTA can measure phase-transition temperatures and identify a material based on its unique calorimetric fingerprint.

NSOM scans a fine-tipped optical probe over the sample surface. Because the aperture is so small and is held so close to the sample surface, the diffraction effects that limit resolution in conventional optical systems do not restrict NSOM resolution. The NSOM probe is made from a single-mode optical fiber that is drawn to an aperture a few nanometers in diameter.

In many cases, accurate measurements depend on the ability to modulate the probe in a particular way to create the desired signal, and the ability to then detect and process that signal. SThM and NSOM again provide instructive examples. In SThM, modulation of the probe heating current controls the amount of heat delivered to the sample and measurements of the probe's resistivity track sample temperature.

NSOM requires a short but constant distance between the probe tip and the sample. This can be accomplished by monitoring the forces generated between the tip and the sample with a laser

a)



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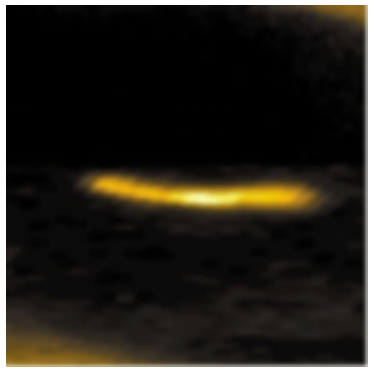
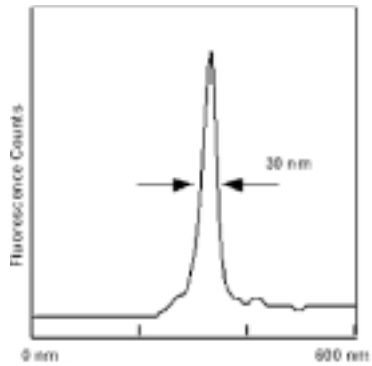





*High quality probe design and control is essential for NSOM experiments. The tuning forks used in the Aurora-2™ provide this as illustrated here.*

*a) excellent low noise performance is evidenced by the shear force topographic image of the organic crystal pentacene clearly showing 1nm steps in the z direction. (Sample courtesy of Tom Jackson, Pennsylvania State University.)*

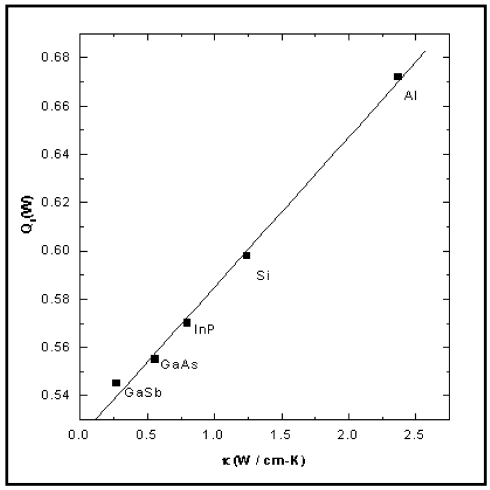
*b) tuning forks with reproducible fiber probes enable the highest resolution optical images as illustrated by the fluorescence image of a single PPEI crystal exhibiting a FWHM of 30nm. (Image courtesy of Paul Barbara, University of Texas, Austin.)*

reflected from the back of the probe. Unfortunately, the light from the laser can interfere with NSOM measurements. ThermoMicroscopes' innovative "tuning fork" technology eliminates the laser and, instead, controls the probe's proximity to the surface by oscillating it laterally while monitoring the shear forces between the tip and the sample.

Measurements made in a vacuum pose a similar problem for monitoring probe deflection. It is difficult to use the AFM light lever technique through the vacuum enclosure. Piezo cantilevers, in which deflections generate an electrical signal in the cantilever itself, provide a viable alternative.

As discussed previously, Near Contact mode can provide quantitative measurements of weak interactions operating over short distances. However, it requires special "soft" cantilevers for its high-frequency, low-amplitude, close-proximity probe modulation. Signal detection is also important in Near Contact mode. While amplitude sensitivity alone is often sufficient to create contrast in Intermittent Contact images, quantitative Near Contact measurements require the additional information provided by phase shift sensitivity.
Scanning Thermal Microscopy (SThM) scans a heated probe over the sample surface and monitors the heating current required to maintain a constant elevated temperature. A

**Thermal imaging of electronic materials**



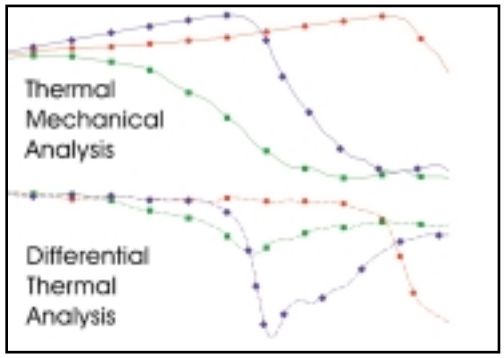

*A simple calibration provides quatitative measurements of local thermal conductivity on electronic materials.*

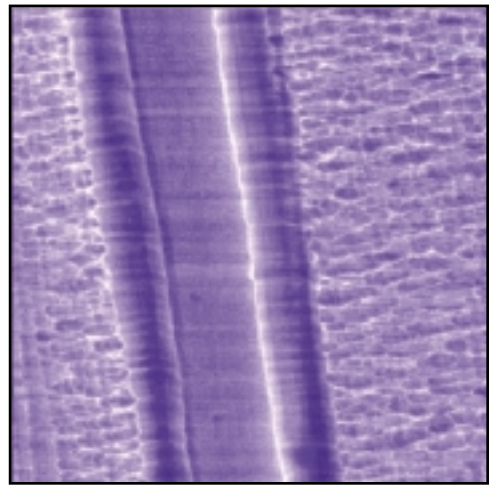
group led by Prof. Fred Pollak at CUNY Brooklyn has applied SThM to the measurement of thermal conductivity in several materials of interest to the electronics industry. They have been able to calibrate their measurements by reference to materials of known conductivity.

GaN is important in the manufacture of devices such as laser diodes and high-power field-effect transistors that would benefit greatly from more efficient heat dissipation. Unfortunately, there is no good substrate on which to grow epitaxial GaN. Sapphire is often used but results in GaN with high dislocation defect density and consequently, poor thermal conductivity.

The CUNY group looked at the thermal conductivity of lateral epitaxial overgrown (LEO) GaN/Sapphire. The LEO technique uses sapphire as a substrate and grows an epitaxial buffer layer of GaN over the substrate surface. Subsequently, a mesh-like mask of SiNx having micron-scale lines and windows is patterned over the buffer layer. More epitaxial GaN is then grown, with growth beginning in the exposed GaN buffer layer in the mask windows, but eventually overflowing the window openings and coalescing with material from neighboring windows. The regions that overlie the SiNx mask grow primarily through lateral epitaxy. Since the dislocation defects do not propagate laterally, these regions have significantly lower defect density and higher thermal conductivity. Only SThM, with its micrometer scale resolution, is capable of measuring the thermal conductivity in these regions.

The CUNY group has also looked at the doping dependence of thermal conductivity of high-vapor-pressure epitaxial-grown n-GaN/Sapphire, deriving a quantitative relationship and concluding that the contribution to increased conductivity from phonon scattering by impurities and free electrons dominates over the electronic contribution.
Typical food packaging films must be mechanically strong, impermeable to oxygen, printable, inert to the food product, and able to stand cooking temperatures; a combination of properties that usually requires a multi-layered



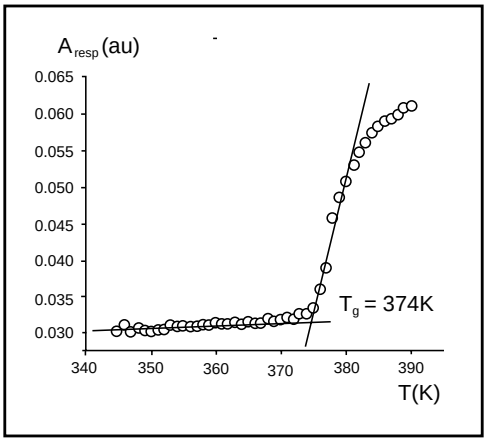
*Food packaging films require multiple layers with different properties. Micro-thermal analysis provides a means of identifying polymeric materials with micrometer scale spatial resolution.*

construction of several materials. The thermal properties of these films are important characteristics for the film designer and also to the investigator seeking to identify the components of an unknown sample. These thin films are very difficult to separate and characterize by conventional bulk analytical techniques. But a group led by Dr. Mike Reading at Loughborough University in the UK uses the thermal probe of the SThM to perform localized thermal analysis on film cross sections with micrometer-scale spatial resolution. After acquiring a thermal or topographic image of the sample and positioning the thermal probe on the layer of interest within the image field, they monitor power consumption (Micro-Differential Thermal Analysis) and mechanical expansion or contraction (Micro-Thermomechanical Analysis) of the sample as a function of probe temperature. The results are directly comparable to the analogous macro-techniques.

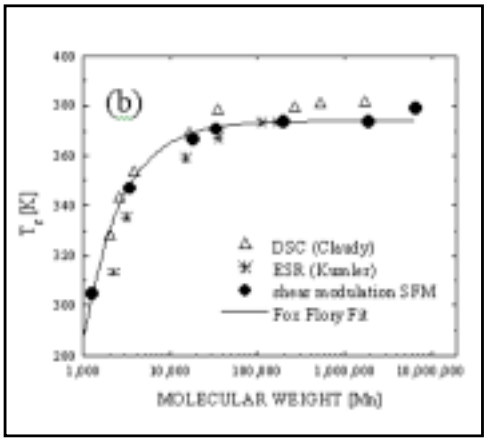
The example shows an image of a cross section of a film composed of HDPE, a tie layer, EVOH, another tie layer, LMDPE, and more HDPE. The softening temperature can be derived from the accompanying Micro-Thermomechanical analysis plot.

Glass transition temperature is certainly one of the most important parameters used to characterize polymers. Dr. René Overney and his group at the University of Washington have devel-

## Determination of glass transition temperature using shear force modulation



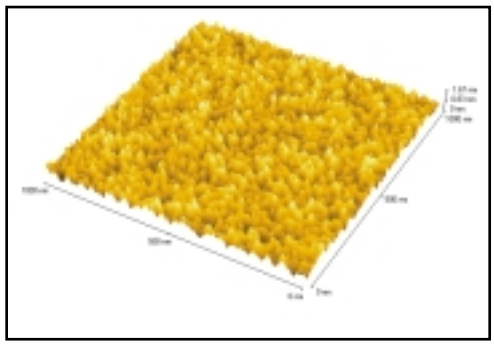

*The glass transition temperature measured on a polystyrene film using shear modulation AFM. [1]*

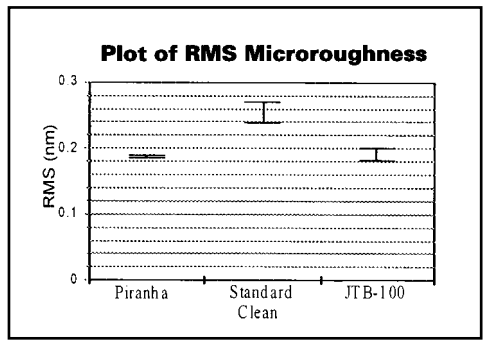



*The glass transition temperature of thick polystyrene films measured at various molecular weights. Results compared well with measurements reported in literature using DSC and ESR.[2, 3, 4]*

oped a technique for determining $T_g$ that they call shear force modulation. In this technique the probe tip is held in contact with the surface in a fixed position and oscillated in the plane of the sample surface. Lateral forces exerted on the tip twist the cantilever and can be detected using the same light-lever mechanism that detects z-direction deflections of the cantilever. The shear force modulation measurement compares the amplitude and phase of the response signal to the driving oscillation. Changes in the sample's mechanical (amplitude response) and viscous (phase response) properties are measured in thermal equilibrium as a heating stage incrementally raises the operating temperature. Similar measurements using conventional force modulation, in which the probe oscillates in the z-direction, in and out of contact with the surface, have been dogged by stability and repeatability problems. These are attributed to the non-intrinsic time varying contact stiffness which makes vertical modulation very rate sensitive. Lateral modulation circumvents these problems by judiciously choosing modulation parameters that keep the tip in no-slip contact with the sample surface. It is like putting your finger gently on the surface of a bowl of gelatin and shaking it very slightly side to side. Stiff gelatin will shake less than soft gelatin. Glass transition temperatures measured with shear force modulation also show a remarkable insensitivity to the rate of the mechanical oscillations within a frequency range of $10^2$-$10^4$ Hz.
David Skee at Mallinckrodt Baker uses AFM to measure micro-surface roughness on silicon wafers. As semiconductor devices become smaller, and the material layers within them


1. R.M. Overney, C. Buenviaje, R. Luginbühl, and F. Dinelli, Journal of Thermal Analysis and Calorimetry, vol 59, (2000) 205-225
2. C. Buenviaje, F. Dinelli, and R.M. Overney in Proceedings of the ACS Fall Meeting, New Orleans, LA August 22-26, 1999.
3. P. Claudy, J.M. Létoffé, Y. Camberlain and J.P. Pascault, Polymer Bulletin, vol 9, (1983) 208-215
4. P.L. Kumler, S.E. Keinath, and R.F. Boyer, J. Macromol. Sci, vol B13, (1977) 631-646





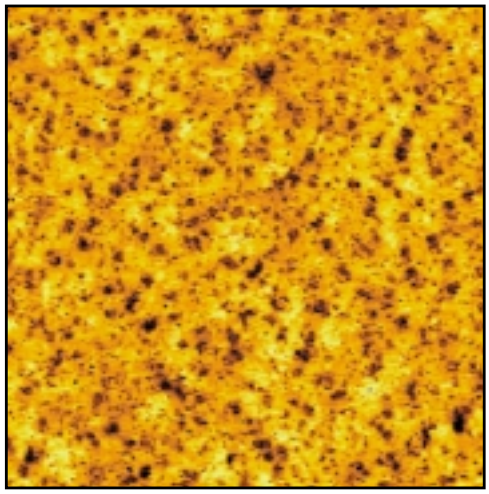

*Quantitative measurements of surface micro-roughness compare the effects of alternative cleaning procedures on a silicon wafer surface. (JTB-100 treatment)*

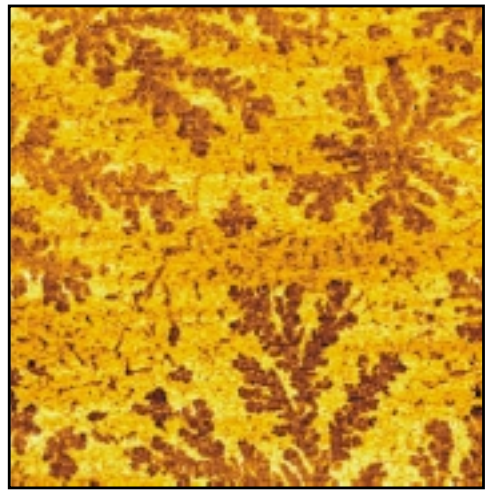
thinner, the roughness of the silicon substrate becomes more important. In particular, surface roughness can cause breakdown in the thin gate oxide that insulates the transistor gate from the source and drain. The measurements are made using Low-Resonant-Frequency (LRF) probes in High Amplitude Resonance (HAR) mode, which, in this case, yields a more representative image of the wafer surface because it penetrates the adsorbed water layer without damaging the silicon surface. The data analysis facility derives repeatable and reliable roughness measurements from a three dimensional topographic map of the scanned area. In this instance, the investigator was able to demonstrate reduced surface damage from a new three-step cleaning process that replaced a conventional four-step process. This resulted in direct savings of time and materials in the cleaning process and, hence, increased yield from the reduced surface roughness.

*Topographic (left) and lateral force (right) images readily visualize the distribution of a wax-like coating.*

Ra

RMS

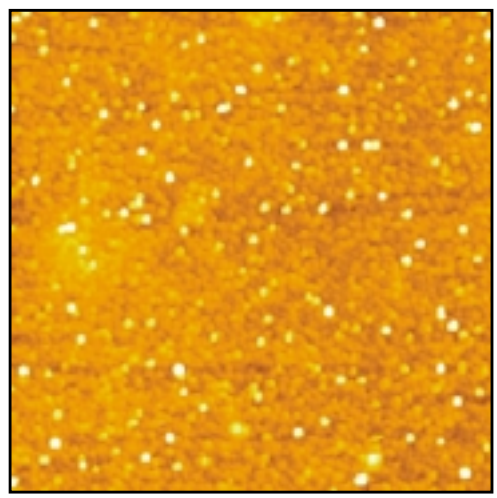




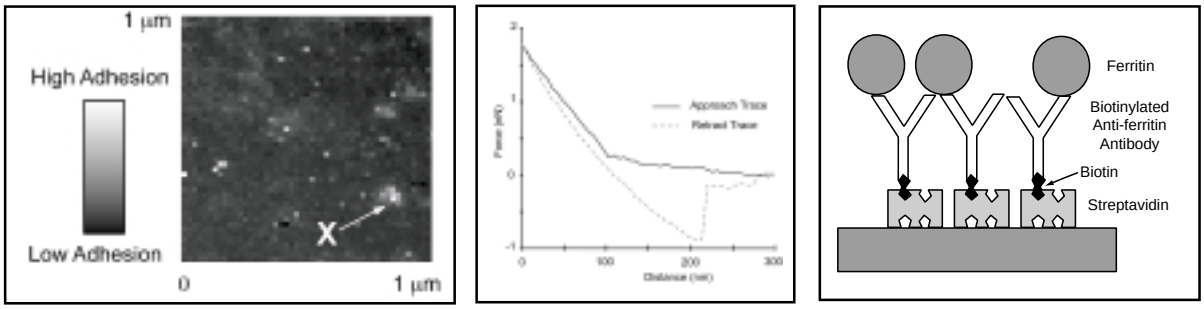
*When calibrated, lateral force techniques can provide quantitative friction measurements. (30 µ scan)*

Today's high-performance coatings are often ultra-thin and may contain nanometer-sized particles. Steve Pratt of Kodak uses AFM extensively to characterize coating materials at the Materials Engineering Surface Metrology Laboratory. Two problems readily solved with AFM are the distribution of thin lubricant coatings and the distribution of nanoparticles within coatings, both of which can be critical determinants of the coating's performance. Lubricant coatings may be only angstroms thick and very difficult to distinguish in topographic images. Lateral Force Microscopy, which measures lateral forces exerted on the probe tip, provides an excellent means of visualizing the lubricant distribution. Combined with the "blind calibration method" developed by the Overney group at the University of Washington, relative lateral force measurements can provide quantitative measurements of frictional forces.

The second problem, nanoparticle distribution, yields readily to a three-dimensional peak counting approach. This technique is derived from two- dimensional peak-counting schemes developed for line profile data but has several advantages. Two-dimensional data do not necessarily cross the apex of a particle, whereas the apex is quite apparent in a three dimensional map. Furthermore, three-dimensional data offer information about the orientation shaped particles. Finally, image processing routines make peak counting and sizing fast and repeatable, allowing the investigator to slice through the data at any height above the surface, counting only peaks of the appropriate size.



*AFM images offer a means of measuring particle size distributions in coating materials. (30 µ*




*The AFM can identify specific biomolecular binding sites (left) by measuring the local adhesive forces (center) betweenthe sample and a funtionalized probe (right).*

## Measuring biomolecular binding forces with force-distance curves

Dr. Saul Tendler and his group at the University of Nottingham in the UK are exploring an exciting new application in biological science that uses the AFM to measure the forces binding biomolecules, such as antigens and antibodies, together. The AFM is sensitive to nanonewton level forces, both attractive and repulsive. By functionalizing the probe (binding the appropriate ligand molecule to it) it is possible to localize receptor molecules bound to the substrate and actually measure the binding forces between the pair. The data constitute a force-distance curve, which plots the z-position of the base of the cantilever (distance) against the positive or negative deflection of the cantilever (force) as the probe approaches and retracts from the sample. Adhesive forces result in a quantifiable negative deflection during the retracting phase as the probe adheres to the surface until sufficient forces build in the cantilever to break it free. The example shows an affinity map of a biotin-streptavidin system in which a receptor site is clearly visible. The plot shows a force distance curve recorded for a ferritin-functionalized probe and anti-ferritin antibody-coated substrate.

## Conclusion

All of the examples offered in the preceding section fall under the broad umbrella of PPT. The thermal imaging and conductivity measurements of GaN and DLN require the special heated thermal probe. The same is required for the Micro-Thermomechanical Analysis and Micro-Differential Thermal Analysis of food packaging films. Shear force modulation requires lateral modulation and amplitude and phase-shift detection capabilities. Microroughness measurement requires the high-amplitude resonance mode and specialized low-resonant-frequency probes. Accurate nanoparticle peak measurement and zooming to revisit counted peaks requires closed-loop feedback on all three piezo axes. Measurements of biomolecular binding forces require functionalized probes and force-distance plotting. Moreover, all of these are excellent examples of the proximity measurements that are now driving the development of Scanning Probe Microscopy.

SPM is evolving along a path typical of new measurement techniques. Accepted initially for its ability to make qualitative observations and to present them as readily interpreted images, it is finding increasingly valuable application as a quantitative measurement tool. This is particularly true in the field of material science where it has transformed many of the traditional macroscopic techniques by giving them microscopic resolution. ThermoMicroscopes' Proximal Probe Technology provides the essential foundation for continuing evolution in this direction. Although imaging will remain an important means of presentation, the future value of the SPM will derive increasingly from its ability to make quantitative measurements.

A picture may well be worth a thousand words, but in today's highly competitive industrial environment the right measurement may be worth a million dollars.

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