When is a Microscope MORE than a Microscope?

Robert J. Plano & Jezz Leckenby*, ThermoMicroscopes
*jezz@thermomicro.com

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 on to 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 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.

The need to quantify specific probe/sample interactions places demands on the SPM that, in many cases, go far beyond the ability to simply sense changes in the interaction and map the changes into an image. Proximal Probe Technology™ (PPT™) is the integrated set of technologies that enables an SPM to make accurate and precise proximity measurements..

SPM BASICS

Before exploring these in more detail let's 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, characterized 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 contact mode atomic force microscopy (AFM) in which the probe remains in constant contact with the sample surface. 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), 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.

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 an SPM 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.

Scan Linearization

Commercially available SPMs use piezoelectric scanners to move the probe relative to the sample or vice versa.. Piezoelectric materials extend or 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 capacitative position sensing and provide the fastest, most accurate corrections available.

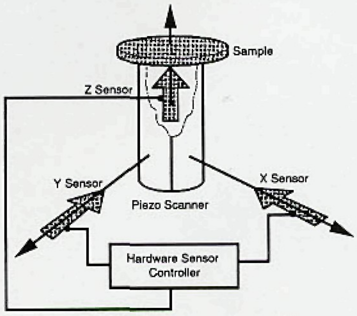

Figure 1: Caption: Real-time scanner position sensing and feedback is essential for accurate scanning

Probe Design

Many measurements require specifically designed probes capable of eliciting and/or detecting the desired interaction with the sample. Scanning thermal microscopy (SThM) and near-field scanning optical microscopy (NSOM) are two examples. SThM

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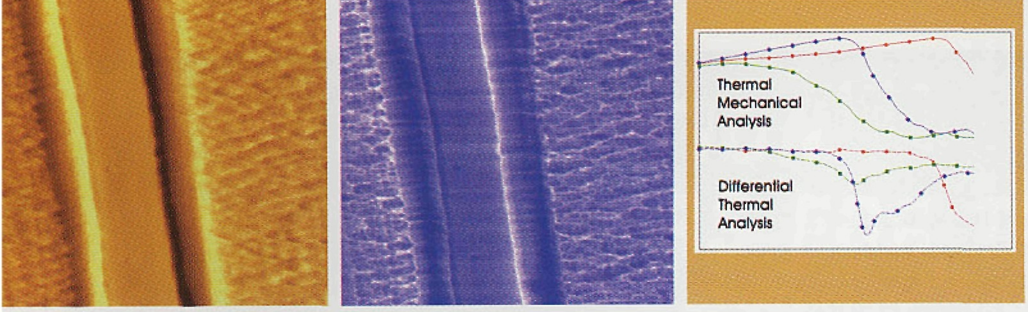
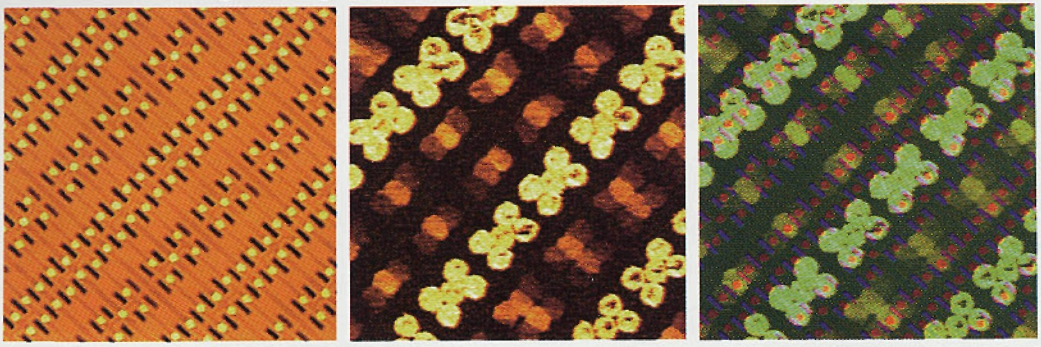
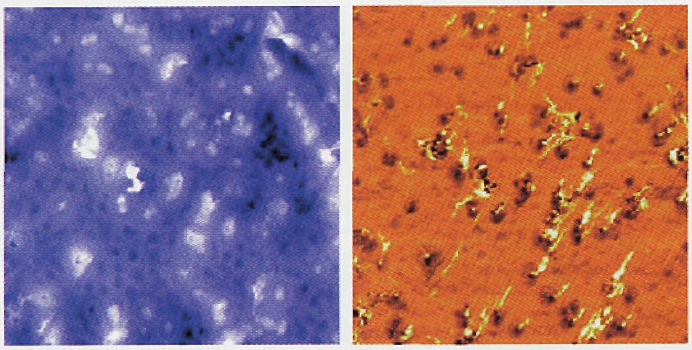


Using topography, thermal conductivity mapping and micro thermal analysis identifies layers in a polymer film. Courtesy of Duncan Price, Loughborough.



Topography and electrostatic force images combine to show misalignment of contacts and implants in SRAM.

When is an SPM more than a microscope?



REGION GROUP	AREA	
	µm²	%
Total area	67.69	100
Silicone lubricant	3.101	4.6
Teflon particles	7.007	10.4

Topography and phase images show area and percent coverage of Teflon® and lubricant in support matrix. Courtesy of Steve Pratt, Kodak.

(When it has PPT.™)

PPT is Proximal Probe Technology.™ And it's only available in Scanning Probe Microscopes from ThermoMicroscopes.

Proximal Probe Technology gives you a whole lot more than just an image. It gives you the full range of proximity measurements you need to get accurate, precise and meaningful data in the engineering terms you recognize. Whether you want to measure friction, stiffness, adhesion, thermal conductivity, electrical or magnetic forces, or a host of other material properties, there's a ThermoMicroscopes system with PPT that's just right for the job. And for process characterization at the nanoscale level, nothing compares to the power PPT gives you.

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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 (TA) 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. TA can measure phase transition temperatures and identify a material based on its unique calorimetric fingerprint.

NSOM scans a finely 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.

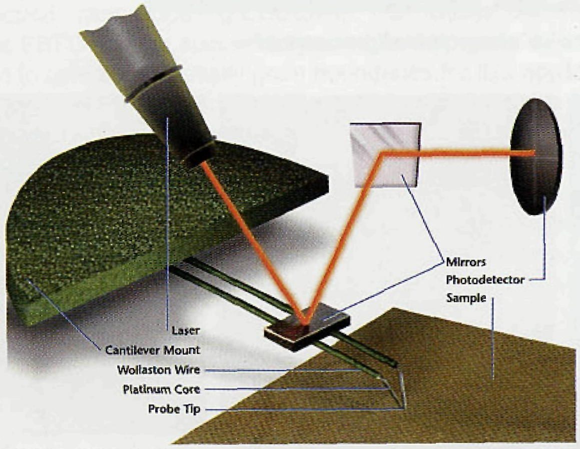

Figure 2: Specialized probes are required to measure many material properties. A thermal probe acts as both a heat source and thermometer to measure local thermal conductivity.

Probe Modulation/Signal Detection

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 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.

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.

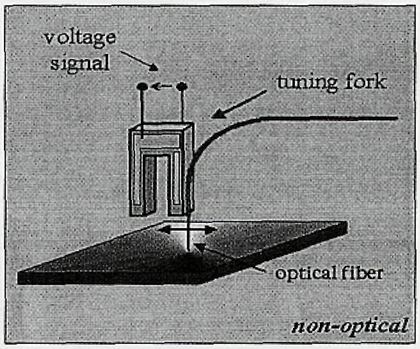

Figure 3: For NSOM measurements an optical fiber, coated and drawn to a very small aperture, is modulated in close proximity to the surface by an electrically driven tuning fork.

APPLICATION EXAMPLES

Localized thermal analysis of polymer films used for food packaging

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 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 uses the thermal probe of the SPM 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.

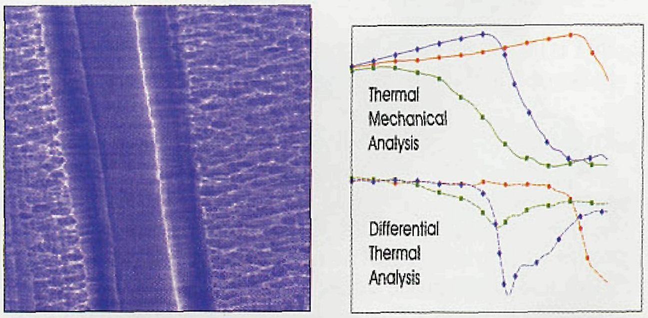

Figure 4: Food packaging films require multiple layers with different properties. Micro thermal analysis provides a means of identifying polymeric materials with micrometer scale spatial resolution.

Micro-metrology of surface coating materials

Today's high-performance coatings are often ultra-thin and may contain nanometer-sized particles. Steve Pratt uses AFM

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- ⬜ Elements currently not detected using X-ray Microanalysis
- 🟥 K alpha energy between 0-10 keV
- 🟧 L alpha energy between 0-10 kev
- 🟩 L alpha energy between 10-20 Kev
- 🟨 M alpha energy between 0-10 kev

Detectors
Pulse Processors
Microanalysis

Digital Imaging
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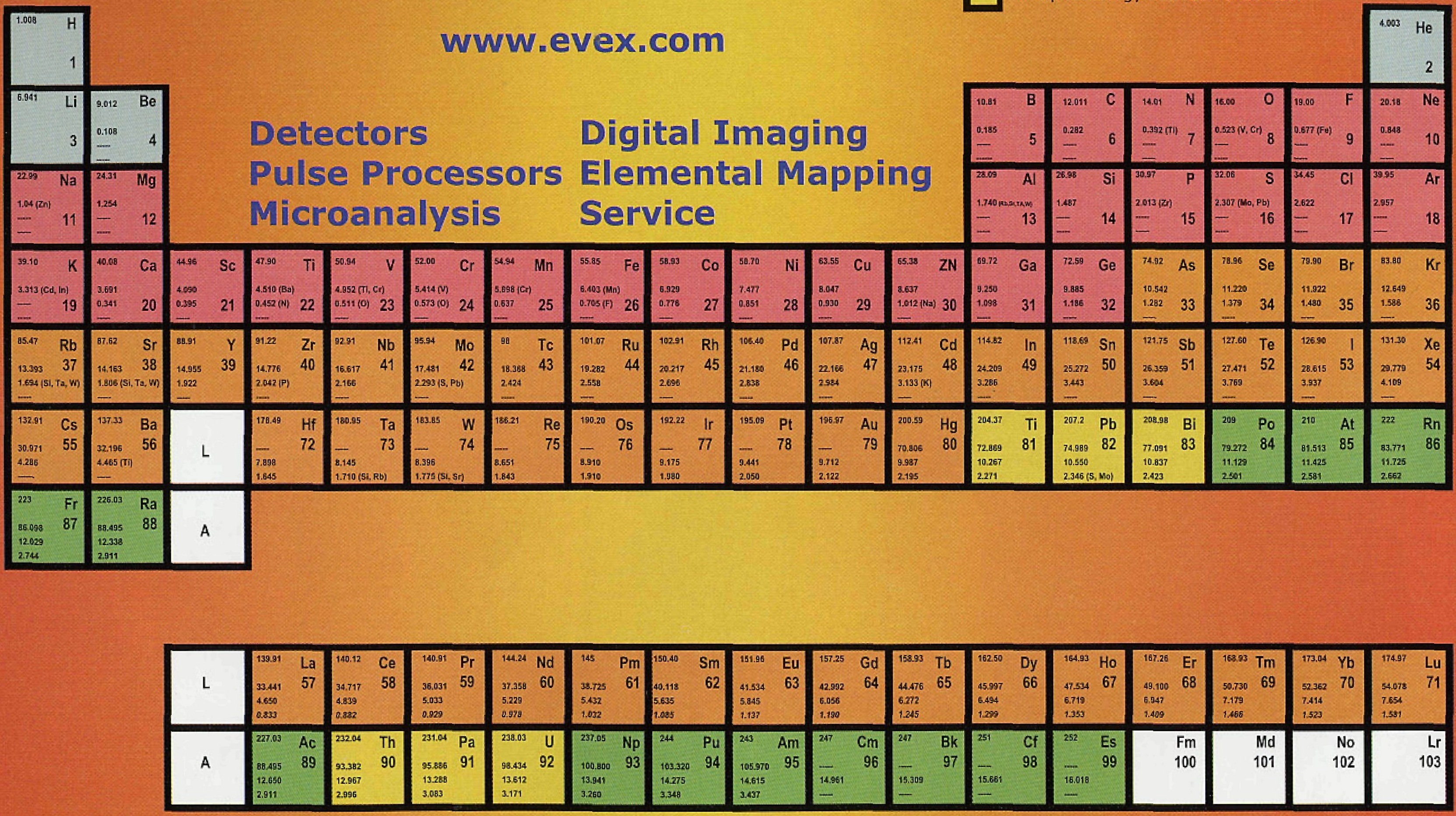
Service



⬜ 1.008 H 1																	⬜ 4.003 He 2
⬜ 6.941 Li 3	⬜ 9.012 Be 4 0.108 — —											🟥 10.81 B 5 0.185 — —	🟥 12.011 C 6 0.282 — —	🟥 14.01 N 7 0.392 (Ti) — —	🟥 16.00 O 8 0.523 (V, Cr) — —	🟥 19.00 F 9 0.677 (Fe) — —	🟥 20.18 Ne 10 0.848 — —
🟥 22.99 Na 11 1.04 (Zn) — —	🟥 24.31 Mg 12 1.254 — —											🟥 28.09 Al 13 1.740 (Rb,Si,TA,W) — —	🟥 26.98 Si 14 1.487 — —	🟥 30.97 P 15 2.013 (Zr) — —	🟥 32.06 S 16 2.307 (Mo, Pb) — —	🟥 34.45 Cl 17 2.622 — —	🟥 39.95 Ar 18 2.957 — —
🟥 39.10 K 19 3.313 (Cd, In) — —	🟥 40.08 Ca 20 3.691 0.341 —	🟥 44.96 Sc 21 4.090 0.395 —	🟥 47.90 Ti 22 4.510 (Ba) 0.452 (N) —	🟥 50.94 V 23 4.952 (Ti, Cr) 0.511 (O) —	🟥 52.00 Cr 24 5.414 (V) 0.573 (O) —	🟥 54.94 Mn 25 5.898 (Cr) 0.637 —	🟥 55.85 Fe 26 6.403 (Mn) 0.705 (F) —	🟥 58.93 Co 27 6.929 0.776 —	🟥 58.70 Ni 28 7.477 0.851 —	🟥 63.55 Cu 29 8.047 0.930 —	🟥 65.38 ZN 30 8.637 1.012 (Na) —	🟥 69.72 Ga 31 9.250 1.098 —	🟥 72.59 Ge 32 9.885 1.186 —	🟧 74.92 As 33 10.542 1.282 —	🟧 78.96 Se 34 11.220 1.379 —	🟧 79.90 Br 35 11.922 1.480 —	🟧 83.80 Kr 36 12.649 1.586 —
🟧 85.47 Rb 37 13.393 1.694 (Si, Ta, W) —	🟧 87.62 Sr 38 14.163 1.806 (Si, Ta, W) —	🟧 88.91 Y 39 14.955 1.922 —	🟧 91.22 Zr 40 14.776 2.042 (P) —	🟧 92.91 Nb 41 16.617 2.166 —	🟧 95.94 Mo 42 17.481 2.293 (S, Pb) —	🟧 98 Tc 43 18.368 2.424 —	🟧 101.07 Ru 44 19.282 2.558 —	🟧 102.91 Rh 45 20.217 2.696 —	🟧 106.40 Pd 46 21.180 2.838 —	🟧 107.87 Ag 47 22.166 2.984 —	🟧 112.41 Cd 48 23.175 3.133 (K) —	🟧 114.82 In 49 24.209 3.286 —	🟧 118.69 Sn 50 25.272 3.443 —	🟧 121.75 Sb 51 26.359 3.604 —	🟧 127.60 Te 52 27.471 3.769 —	🟧 126.90 I 53 28.615 3.937 —	🟧 131.30 Xe 54 29.779 4.109 —
🟧 132.91 Cs 55 30.971 4.286 —	🟧 137.33 Ba 56 32.196 4.465 (Ti) —	L	🟧 178.49 Hf 72 — 7.898 1.645	🟧 180.95 Ta 73 — 8.145 1.710 (Si, Rb)	🟧 183.85 W 74 — 8.396 1.775 (Si, Sr)	🟧 186.21 Re 75 — 8.651 1.843	🟧 190.20 Os 76 — 8.910 1.910	🟧 192.22 Ir 77 — 9.175 1.980	🟧 195.09 Pt 78 — 9.441 2.050	🟧 196.97 Au 79 — 9.712 2.122	🟧 200.59 Hg 80 70.806 9.987 2.195	🟨 204.37 Ti 81 72.869 10.267 2.271	🟨 207.2 Pb 82 74.989 10.550 2.346 (S, Mo)	🟨 208.98 Bi 83 77.091 10.837 2.423	🟩 209 Po 84 79.272 11.129 2.501	🟩 210 At 85 81.513 11.425 2.581	🟩 222 Rn 86 83.771 11.725 2.662
🟩 223 Fr 87 86.098 12.029 2.744	🟩 226.03 Ra 88 88.495 12.338 2.911	A															
		L	🟧 139.91 La 57 33.441 4.650 *0.833*	🟧 140.12 Ce 58 34.717 4.839 *0.882*	🟧 140.91 Pr 59 36.031 5.033 *0.929*	🟧 144.24 Nd 60 37.358 5.229 *0.978*	🟧 145 Pm 61 38.725 5.432 *1.032*	🟧 150.40 Sm 62 40.118 5.635 *1.085*	🟧 151.96 Eu 63 41.534 5.845 *1.137*	🟧 157.25 Gd 64 42.992 6.056 *1.190*	🟧 158.93 Tb 65 44.476 6.272 *1.245*	🟧 162.50 Dy 66 45.997 6.494 *1.299*	🟧 164.93 Ho 67 47.534 6.719 *1.353*	🟧 167.26 Er 68 49.100 6.947 *1.409*	🟧 168.93 Tm 69 50.730 7.179 *1.466*	🟧 173.04 Yb 70 52.362 7.414 *1.523*	🟧 174.97 Lu 71 54.078 7.654 *1.581*
		A	🟩 227.03 Ac 89 88.495 12.650 2.911	🟨 232.04 Th 90 93.382 12.967 2.996	🟨 231.04 Pa 91 95.886 13.288 3.083	🟨 238.03 U 92 98.434 13.612 3.171	🟩 237.05 Np 93 100.800 13.941 3.260	🟩 244 Pu 94 103.320 14.275 3.348	🟩 243 Am 95 105.970 14.615 3.437	🟩 247 Cm 96 — 14.961 —	🟩 247 Bk 97 — 15.309 —	🟩 251 Cf 98 — 15.661 —	🟩 252 Es 99 — 16.018 —	Fm 100	Md 101	No 102	Lr 103

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https://doi.org/10.1017/S1551929500052792 Published online by Cambridge University Press

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extensively to characterize coating materials at Kodak's Materials Engineering Laboratory 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.

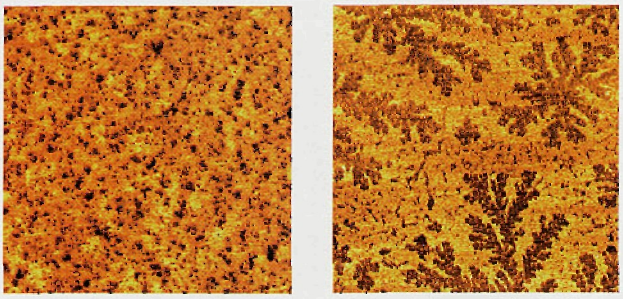

Figure 5: Topographic (left) and lateral force (right) images readily visualize the distribution of a wax-like coating. When calibrated, lateral force techniques can provide quantitative friction measurements.

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 does not necessarily cross the apex of a particle, whereas the apex is quite apparent in a three dimensional map. Furthermore, three-dimensional data offers information about the orientation of 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.

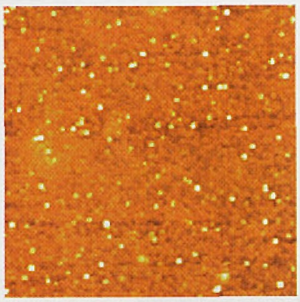

Figure 6: AFM images offer a means of measuring particle size distributions in coating materials.

Measuring biomolecular binding forces with force-distance curves

Dr. Saul Tendler and his group at the University of Nottingham are exploring an exciting new application in pharmaceutical 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.

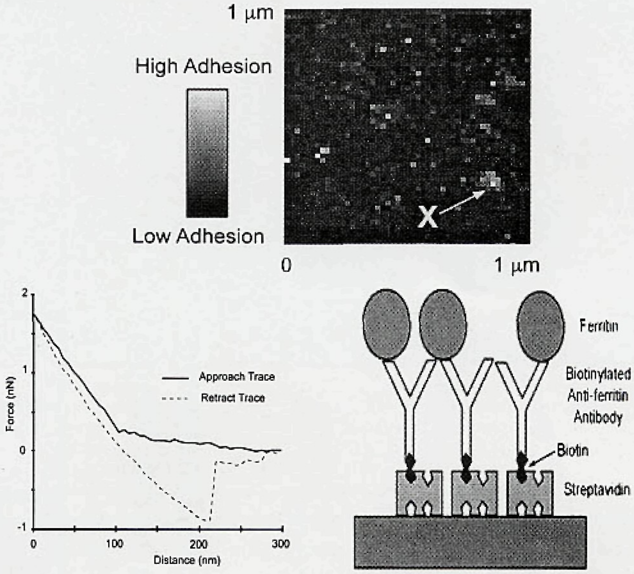

Figure 7: The AFM can identify specific biomolecular binding sites (upper) by measuring the local adhesive forces (lower left) between the sample and a funtionalized probe (lower right).

CONCLUSION

The examples offered above all fall under the broad umbrella of PPT. The micro-thermomechanical analysis and micro-differential thermal analysis of food packaging films require the special heated thermal probe. 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 bucks.