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Recent progress in microthermal analysis

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A characterization technique combining scanning thermal imaging (SThM) with thermal analysis[1–4] has been developed based on an atomic force microscope (AFM) in which the normal probe has been replaced by one with a resistive heater at the tip. The tip can therefore supply heat when a current is passed through it and also measure temperature by measuring the resistance of the probe. For the first time it makes possible imaging on the basis of both ac and dc thermal properties (where the temperature of the tip is maintained at a constant average temperature while applying a temperature modulation) combined with the ability to perform thermal analysis on any selected small area

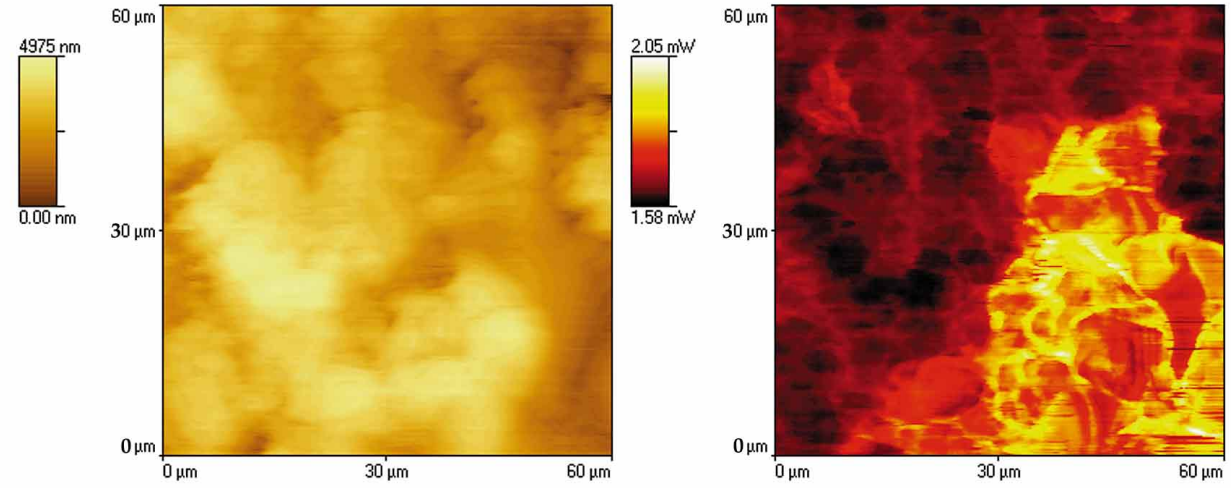

Figure 1 *Topographic (left) and dc thermal (right) images of acetaminophen analgesic tablet. (Reproduced with permission from Institute of Materials.)*

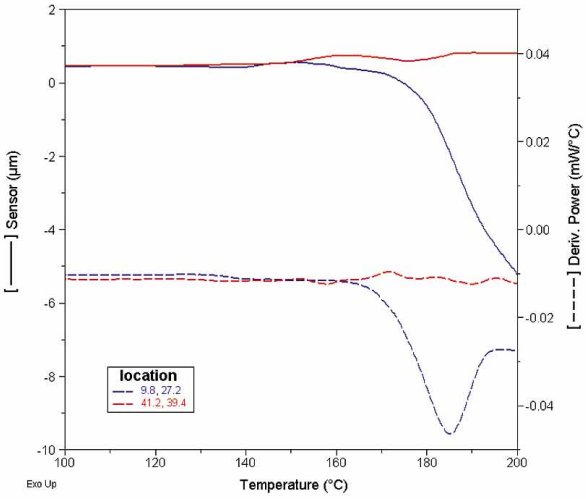

Figure 2 *Localized thermal analysis of low (blue curves) and high (red curves) thermal conductivity regions of tablet in Figure 1 (solid lines: micro-TMA; broken lines; micro-MTDTA power). (Reproduced with permission from Institute of Materials.)*

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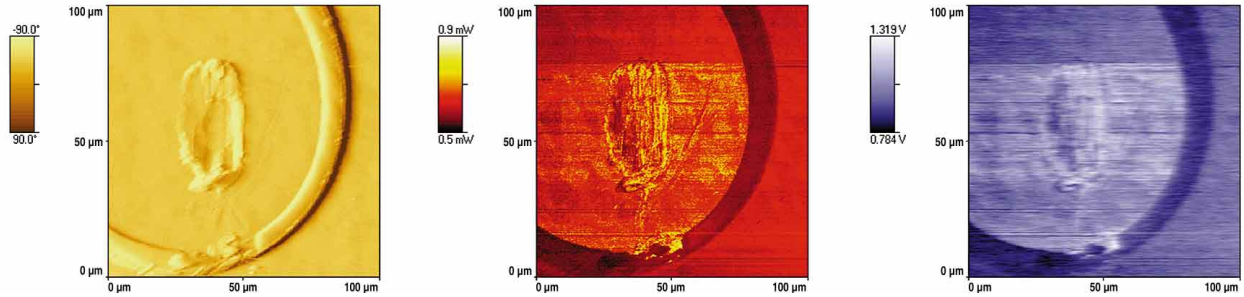

Figure 3 *Left to right: topography, dc thermal, and ac (30 kHz) thermal images of light-emitting diode #1. Scratches in the center of the image are the result of the removal of a gold contact wire.*

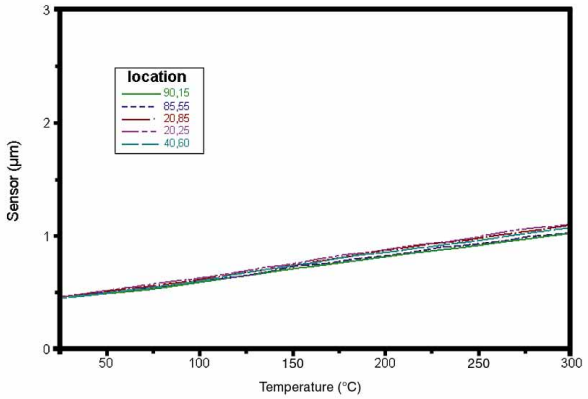

Figure 4 *Localized thermal analysis (micro-TMA) of different areas of Figure 3.*

using both a mechanical measurement (microthermomechanical analysis [micro-TMA]) and micro-modulated temperature differential thermal analysis (DTA) measurement (micro-MTDTA). *Figure 1* shows the topographic and dc thermal images of an acetaminophen tablet, which were obtained simultaneously. The topography does not enable the drug to be differentiated from the excipient, whereas the thermal image clearly shows two distinct phases. The probe was then placed on the bright area and the dark area, and thermal analysis experiments were carried out as shown in *Figure 2*. The light-colored material exhibits no transitions, whereas the dark material shows a melting transition in both the micro-TMA and micro-MTDTA signals. It can be concluded that the light area is the excipient and the dark area is the drug. This ability to image structure and identify materials from their thermal behavior has a wide range of applications in materials and pharmaceutical science. The instrument has been commercialized by **TA Instruments Inc.** (New Castle, DE).

This paper presents an interesting new application for semiconductor devices and an extension of microthermal analysis in which the entire sample is heated using a hot stage.

Use of micro-TA on light-emitting diodes

Figure 3 shows the topographic, dc thermal, and ac thermal images for a light-emitting diode. There is little thermal contrast between the circular feature and its surroundings. Thermal scans carried out inside and outside of this feature can be seen in *Figure 4* and exhibit no differences in thermal expansion behavior. *Figure 5* shows a very similar component that failed in service. These images show significant differences in thermal contrast between the circular component and its surroundings. This observation is reinforced by the thermal scans in *Figure 6*, in which the measurements outside of the circle demonstrate a lower thermal expansion than the measurements inside. This is a good example of ways in which thermal scans can be used to study differences in materials, even in the absence of transitions. In this case, differences in thermal expansion coefficient led to failure of the component.

Use of pulsed force mode with a hot stage

The gathering of information from force distance curves has recently been automated[5] and made faster using the pulsed force method, which enables images to be generated of indentation and pull-off force at normal AFM scanning speeds. In *Figure 7*, two pull-off force images obtained at two different temperatures are shown for a spun-coated blend of poly(methyl methacrylate) (PMMA) and polystyrene (PS). Although the pull-off force is often thought to measure adhesion, in fact it is strongly influenced by the viscoelastic properties of the substrate. At 50 °C, there is little difference between the occluded phase and the matrix, whereas at 110 °C, the pull-off force required for the occluded phase increases dramatically. Since the intrinsic attraction between the tip and a given phase would not normally undergo a dramatic change with temperature, it can be concluded that the observed change is due to a change in its viscoelastic properties. The likely explanation is that it has undergone a glass transition; thus, it is the lower Tg (glass-transition temperature) material that forms the occluded phase (in this case, macrothermal analysis shows it to be the PS). In this way, the contrast between phases can be increased and phases can be identified.

This is a general method for characterizing systems that do not undergo significant morphological

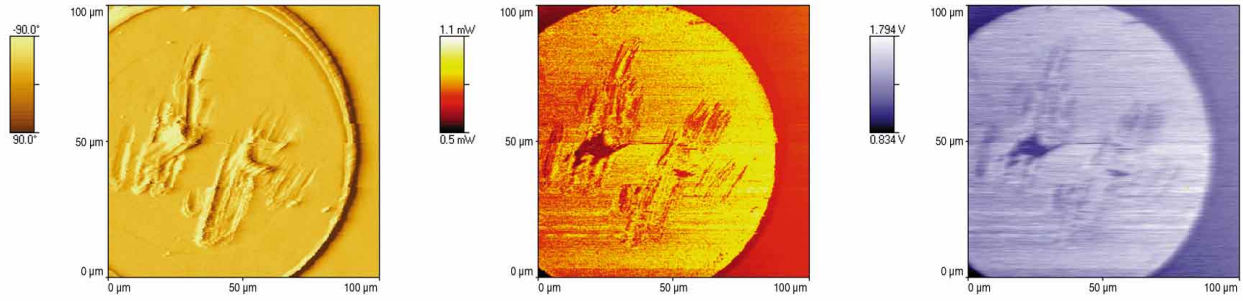

Figure 5 *Left to right: topography, dc thermal, and ac (30 kHz) thermal images of light-emitting diode #2. Note the high contrast in thermal properties between the inside and outside of the structure compared to Figure 3. (Reproduced with permission from Wiley-VCH.)*

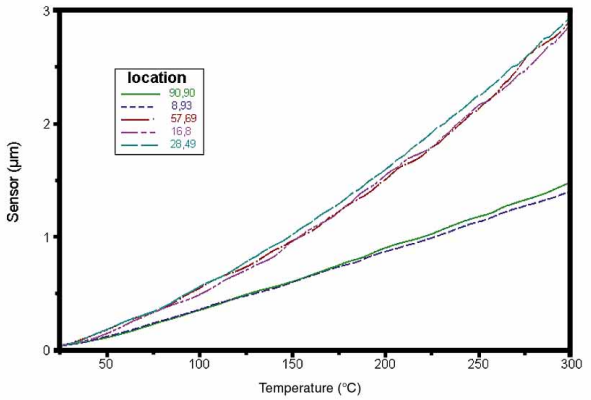

Figure 6 *Localized thermal analysis (micro-TMA) of different areas of Figure 5. Note the difference in thermal expansion between areas corresponding to those with different thermal image contrast. (Reproduced with permission from Wiley-VCH.)*

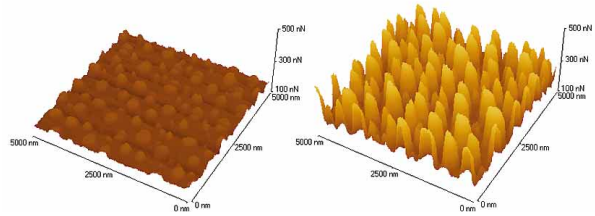

Figure 7 *Pulsed force mode (pull-off force) images of a polystyrene/poly(methyl methacrylate) blend at 50 °C (left) and 110 °C (right) showing the increase in pull-off force between the polystyrene domains and the probe tip as the polymer is heated above its glass transition temperature.*

change as they are heated. The advantage in this case is that normal AFM resolution can be achieved because the tip is a standard one. Normally the use of local heating using a heated tip is the preferred approach, but the use of a hot stage can serve as an alternative in some cases.

Conclusion

A mounting body of evidence shows that SThM and microthermal analysis have a wide range of applications in materials science, pharmaceuticals, microelectronic devices, and even biological systems. Either the sample can be locally heated by the tip, the entire sample can be heated using a hot stage, or combinations of the two can be used. The use of temperature as a variable can increase the amount of information that can be obtained even when using standard AFM modes of imaging, as shown in the example given above using pulsed force measurements. In addition to physical characterization using calorimetric and mechanical measurements, plans are under way to make chemical analysis possible using incident IR radiation to produce local IR spectra and local pyrolysis with analysis of the evolved species by GC-MS. The group of microthermal methods is growing into a very powerful and general tool for high-resolution microcharacterization.

References

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