Keysight Technologies

Differentiating Surface Mechanical Properties with Dynamic Lateral Force Microscopy

Application Note

Introduction

Atomic Force Microscopy (AFM) has proven itself to be an effective and versatile tool for the comprehensive characterization of materials with a very high spatial resolution because it can reveal not only their surface structural information but also the local variations of their mechanical, electric and magnetic properties ranging from sub nanometer to micrometer scales from the tip-surface interactions. The basic and most popular AFM imaging is certainly by the contact and intermittent modes that sense mainly the tip-sample mechanical interaction in the vertical and/or lateral direction. As the derivatives from them, the lateral force mode (LFM) is developed with the contact mode, the amplitude and phase imaging comes with the intermittent contact mode. The intermittent contact imaging where an AFM cantilever is mechanically oscillated near its resonance frequency and the AFM tip taps the sample surface with negligible lateral force is particularly favored for imaging soft and/or heterogeneous surfaces because it gives not only a better topography resolution with less damage to the tip and the surface due to the elimination of lateral shear force that is present in the contact mode imaging but also the complementary amplitude and phase information arising from the cantilever modulation change that is perpendicular to the surface. However for surface studies of frictional and tribological properties of viscoelastic materials the contact mode AFM and LFM have played an essential role because regions of enhanced friction force have greater viscoelastic dissipation under sliding contact [1–3]. LFM is also used for obtaining edge enhanced imaging of any surfaces.

As an extension of the contact mode technique, the force modulation mode applies a modulation signal at an off-resonant frequency of typically a few to tens of KHz either to the Z piezoelectric scanner or to a separate Z piezoelectric actuator, giving a small modulated vertical force while the tip is in contact with the surface. Different stiffness and adhesion arising from various regions of the surface can cause the amplitude of the AFM cantilever deflection to change at the frequency of modulation, giving a measure of elastic and viscoelastic properties of the soft materials such as polymers, organic films and biological samples[4–6]. This force modulation microscopy expands the contact mode imaging capability in a way similar to the amplitude imaging by the intermittent contact mode mentioned earlier. Another extension of the contact mode is called the shear modulation force microscopy. Analogous to the force modulation mode, the off-resonance sinusoidal drive signal is applied to X piezoelectric scanner in the lateral direction parallel to the plane of the sample surface. The lateral deflection amplitude and phase of the cantilever from outputs of a lock-in amplifier measures the dynamic torsional force on the tip that is sensitive to the lateral surface physical properties. Variables that can affect this technique including but not limited to surface chemistry, probe shape and size, cantilever stiffness, applied contact force, amplitude, frequency and direction of the lateral modulation8. During the past decade shear modulation force microscopy has been used effectively to measure surface viscoelastic properties and the stick-to-slide transition of soft materials[7] and the glass transition temperature of the polymer thin films[8–10].

Instrumentation

Keysight Technologies, Inc. Dynamic Lateral Force Microscopy (DLFM) is an improved version of the traditional shear modulation force microscopy mentioned earlier with a nose cone accessory called DLFM nose cone that can be attached to any platform of AFM/SPM that Keysight manufactures. The DLFM nose cone has a built-in dedicated piezoelectric actuator that provides an oscillatory force in the tip fast scan (x) direction parallel to the sample surface and the lateral modulation signal will not cause a spurious excitation of the X scanner mechanical resonance even at high frequency.

Here we performed DLFM using the latest Keysight 7500AFM with a DLFM nose cone. The 7500AFM can allow for interchangeable and easy-to-mount nose cones to be attached to the high performance and low noise 7500 closed loop scanner to perform multiple imaging modes. While the normal contact force is maintained constant to the surface by the feedback (DC deflection) to get the topography and LFM images, the lateral oscillation amplitude and phase (AC deflection) can be acquired through the AC Mode lock-in amplifier (either an AAC or AAC3 controller). For the experiments in this note we used force modulation cantilever and typically set the lateral drive frequency well off the lateral resonant frequency of the cantilever.

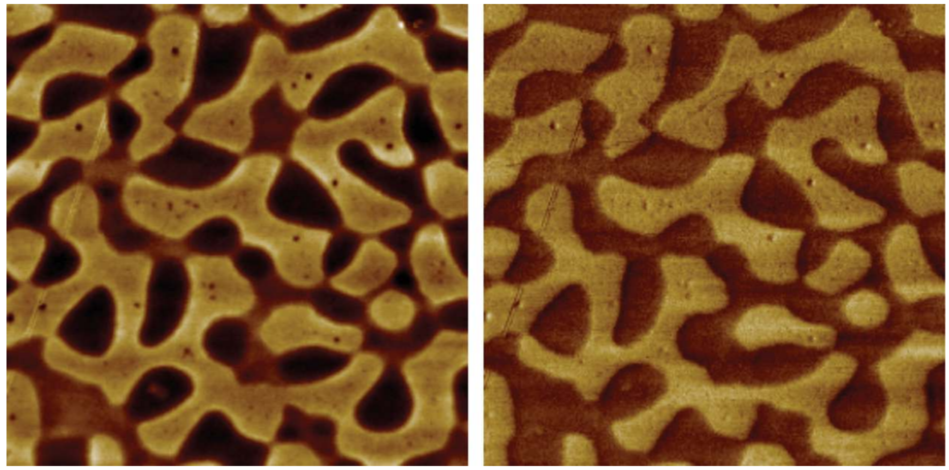

Figure 1. Contact mode topography (left) and DLFM amplitude (right) images of PS-PMMA block copolymer surface at 5µm scan

Resolving the Heterogeneous Polymer Components through Their Physical Properties

Amplitude and phase imaging by the normal AC mode AFM (intermittent contact or non-contact) of the block copolymers have been well known to be able to reveal structural information about the components or phases due to their elasticity or stiffness differences. The amplitude and phase signal from the DLFM may well respond to the same mechanical property differences in these structurally heterogeneous materials. Figure 1 shows the topography and amplitude images by DLFM of a 20-nm thick film of PS-PMMA (polystyrene and polymethyl methacrylate with a weight ratio 3:7) which was spin-casted onto a Si substrate. Both images resolve well the microphase separation with islands and holes that is commonly seen in diblock copolymer thin films. The height difference between the two phases in the topography can be attributed to the molecular chain length difference of the two components oriented in the direction perpendicular to the underlying substrate surface[11]. But we cannot rule out the contribution from a physical property standpoint to the height difference because under a certain contact force the tip indention on the two components would be different and it is known that PMMA phase is relatively stiffer than the PS phase. The PMMA phase also shows high lateral deflection amplitude in the DLFM amplitude image because of its slightly higher shear modulus and microhardness as compared to the PS phase[12], leading to less viscoelastic dissipation hence smaller friction.

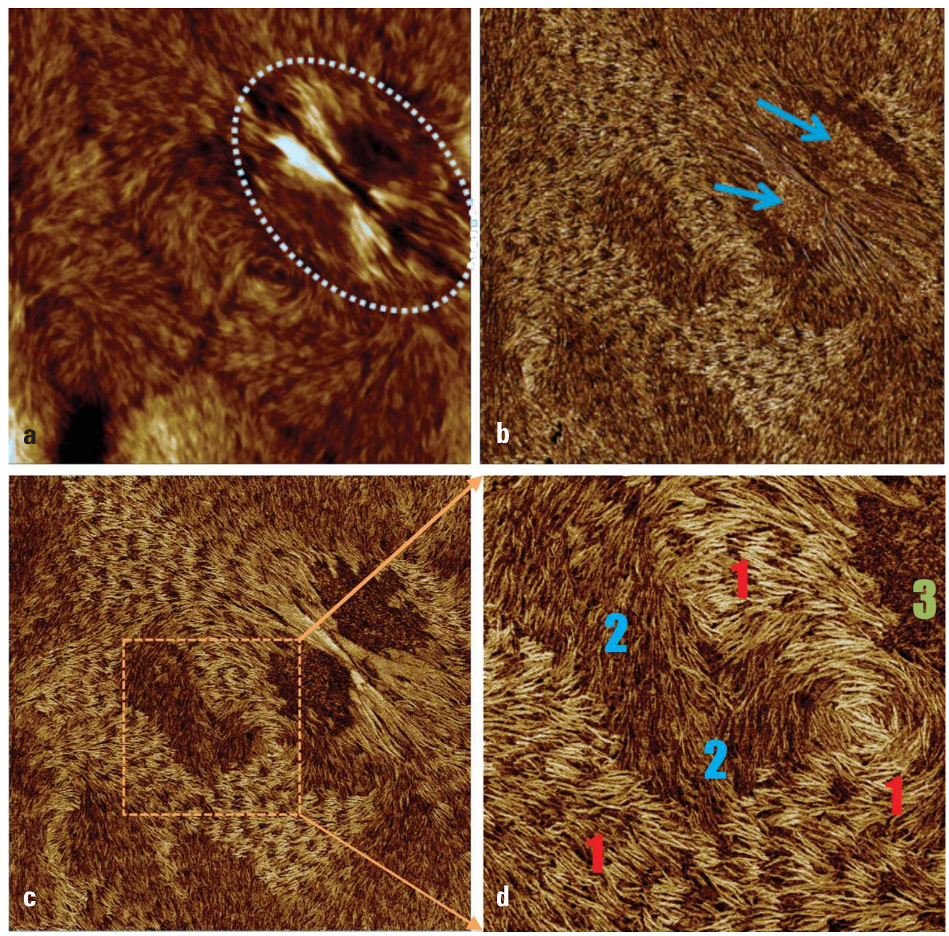

Figure 2. Contact mode topography (a), DLFM amplitude (b) and phase (c) images of LDPE surface at 10µm scan. (d) is a zoom-in image at 4µm scan from (c) and regions of different phase contrast are marked by 1, 2 and 3.

The example of PS-PMMA sample is a typical case where the physical property difference of the two phases comes from their distinctive chemical identities. Structural inhomogeneity is also common in semicrystalline polymers due to the coexistence of different states of the same material. Such an example can be visualized with a low density polyethylene (LDPE) sample prepared from melt by the DLFM imaging as shown in Figure 2.

Figure 2(a) shows that under the contact force the tip penetrates the thin surface amorphous polymer layer and reveals the morphology of crystalline and amorphous components commonly seen from the LDPE surface consisting of spherulites with elevated centers and lower domains with their borders. A typical spherulite feature of about 4–6 µm in size is marked by the dotted oval circle. The rest domains appear to show bundles of harder crystalline lamellae (higher in height) separated by softer amorphous polymer (lower in height). This is similar to what we see with PS-PMMA in Figure 1 when the two components of different stiffness respond differently to the normal tip force leading to the height contrast. The simultaneously acquired LFM image (not shown here) generally shows similar features to the topography one without gaining any additional detail.

However it is rather interesting to see that the DLFM amplitude and phase images in Figure 2(b)–(d) reveal regions of distinctively different lamellar orientation and contrast that are not so clearly seen in topography and LFM. This is the result of higher sensitivity from the dynamic frictional response to the viscoelastic property difference of the two components — the soft amorphous polymer has a greater lateral loss modulus and leads to more strain energy dissipation, hence higher friction and darker in contrast, as compared to the rigid lamellae. Furthermore, regions with different levels of amplitude and phase contrast are clearly distinguishable that are not consistent to the height information from the topography. In order to best illustrate this, Figure 2(d), a zoom-in phase image from an area marked by the orange dotted line in Figure 2(c), gives 3 levels of color contrast marked by 1, 2 and 3 in the sequence of their brightness from strong to weak. One can see that the brightest region 1 is primarily dominated by lamellae orientated parallel or close to the tip oscillation direction, the less bright region 2 is primarily dominated by lamellae orientated perpendicular to the tip oscillation direction, and the least bright region 3 is primarily dominated by lamellae orientated perpendicular to the surface. Since this contrast difference did not seem to change in the repulsive force regime when we varied force setpoint, drive frequency and amplitude over some range we believe that the contrast difference is primarily due to the modulation response to the lateral stiffness over the scanned regions. When the lamellae are oriented close to the modulation direction (same as the fast scan X axis) the tip interacts with laterally stiffer lamellae in their length axis and hence results in the least tip drag, amplitude reduction and phase lag, thus the brightest contrast. In other worlds the region 1 represents the least shear force, adhesion and loss modulus. On the other hand, when the lamellae are oriented perpendicular or at a very large angle to the tip oscillation direction, the tip senses an overall less stiffer region with an increased frictional response. Intuitively it is easy to understand that in the width direction of the lamellae they are more sandwiched by the soft amorphous polymer and hence more flex under the lateral oscillated tip. This is what we see in the region 2 that represents more loss modulus. However the region 3 appears to show overall the least stiffness and highest loss modulus when the lamellae are populated with their length axis perpendicular to the imaging surface shown as the bright dots imbedded in the dark amorphous domains. Such a lamellar structure is inherently the most flex under the lateral modulation force. In fact the level of fine detail about individual lamellar feature and orientation can be best evidenced by the lateral amplitude response, Figure 2(b). Correlating the region 3 in Figure 2(d) to its position in Figure 2(b), for example, Figure 2(b) not only shows the orientation of lamellar structure that is vertical to the surface it can further distinguish two areas close to the center of the spherulite that have slightly brighter amplitude contrast and are somewhat more densely packed (marked by blue arrows) than the rest within the region 3. This seems to suggest that the amplitude response is slight more sensitive under this particular operating condition of non-resonant modulation. In addition the lateral deflection amplitude, as compared to the lateral phase, is more sensitive to the edge effect from the lamellae that are oriented either edge-on (seen as brighter thin strips parallel to the surface) or perpendicular to the surface (seen as brighter tiny dots) over the entire scanned area. The detail of very long diagonal thin lines of lamellar feature across the top of the spherulite can be better resolved in Figure 2(b) as compared to Figure 2(c).

Probing the Decoupled Graphene Regions on the Surface of Graphite

Graphene, a fundamental building block of all graphitic materials, is a novel two-dimensional carbon material consisting of a single to a few layers of atomically thin carbon sheets. It has drawn intensive research and industrial interest in recent years due to its extraordinary electronic properties and as the potential nanomaterial for highly efficient ultra-thin nanoelectronic devices.

A few dynamic AFM modes, such as amplitude and phase imaging that is very sensitive to relative changes in local mechanical properties, and surface potential and capacitance gradient imaging that is very sensitive to relative changes in local electrical properties, have been demonstrated with Keysight AFM for differentiating single layer and a few layers of graphene and their interlayer interactions[13].

It has been reported that when the stacking order in the c direction of the graphene with respect to the graphite substrate is random the electronic structure of the graphene can decouple electronically from the graphite substrate[14] or physically detached from the Bernal-stacked layers underneath[15–16]. Various spectroscopic techniques such as infrared spectroscopy, Raman spectroscopy and scanning tunneling spectroscopy have been used to distinguish domains of graphene with different levels of decoupling from the graphite that lead to the changes in its optical or electromagnetic properties. However such different levels of layer decoupling could result in some local variation in the mechanical properties (stiffness, adhesion and shear force) of the graphene surface.

Figure 3 shows the contact mode topography and DLFM amplitude images of a HOPG surface where one can see that there are areas of dark amplitude contrast on the graphite terraces in the amplitude image that are not seen in the topography image. Given the fact that there is no height difference contributing to the lateral deflection change within the same

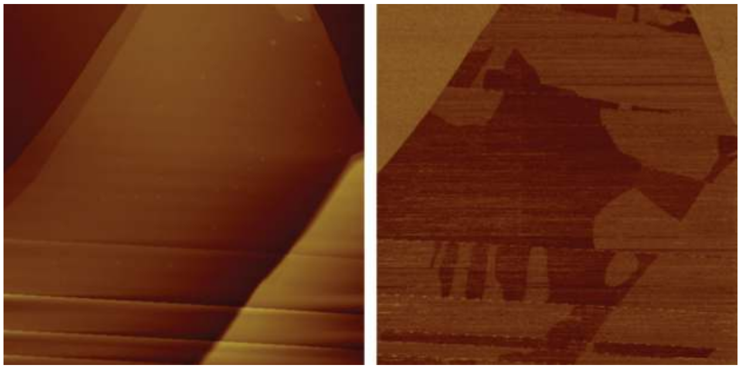

Figure 3. Contact mode topography (left) and DLFM amplitude (right) images of HOPG surface at 30 µm scan.

terrace, these areas with darker contrast represent regions of relatively high shear force and relatively low lateral stiffness which can be the result of some physical structural variations underneath the HOPG surface, e.g., the existence of graphene layer decoupling. In a separate study with a HOPG surface, the result of which will be reported elsewhere, certain regions with dark DLFM amplitude contrast were found to correlate well to the finding from the Raman experiment that indicated underlying decoupled graphene domains. Thus the DLFM technique clearly holds a great potential as an effective and highly sensitive tool to probe the physical structure difference beneath the materials surfaces.

Summary

In the work of this note Dynamic Lateral Force Microscopy (DLFM) was used to differentiate polymer components with heterogeneous physical properties arising from either the different chemical compositions or the different phases with the same chemical composition and to identify regions of the physical decoupling of graphene layers underneath the graphite surface. DLFM amplitude and phase imaging is highly sensitive to small variations of surface viscoelastic and tribological properties and can hence serve as a very effective tool complementing other AFM-based techniques for the investigation of materials surfaces at the nanoscale.

KEYSIGHT TECHNOLOGIES

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