CR Storage Modulus

CR Loss Modulus

FASTForce Volume CR diagram

Quantitative Measurements of Elastic and Viscoelastic Properties with FASTForce Volume CR

Quantitatively characterizing nanomechanical properties has always been a holy grail for atomic force microscopy. This application note discusses some of the industry's previous attempts at quantitative nanomechanical measurement, and introduces a method of performing contact resonance that overcomes many of the previous hurdles of the technique. Implementation, operation, and application examples of FASTForce Volume CR (contact resonance) are discussed, showing that the technique offers a fast, accessible, and easy-to-use means for quantitative characterization of elastic and viscoelastic properties.

Introduction

Given the inherently mechanical interaction between an AFM tip and sample, it is not surprising that a number of methods have evolved that take advantage of this interaction to measure material properties. Tapping mode, which has been around for over 25 years and is the most common AFM imaging method, includes an equally popular phase channel that generates qualitative contrast from material properties. However, truly quantitative nanomechanical measurements have proven to be much more challenging for tapping mode. Over the years, a number of other techniques have been developed for the quantitative measurement of mechanical properties. Methods such as PeakForce QNM and Force Volume have emerged to successfully quantify modulus and other mechanical properties.

Another important nanomechanical AFM capability is contact resonance, a resonant dynamic contact-based method. In this method, the cantilever vibrates while in contact with the surface where mechanical excitation occurs either through the tip[1] (ultrasonic AFM) or through the sample (atomic force acoustic microscopy).[2] Contact resonance was originally developed to measure elastic properties of stiff materials with improved sensitivity[1,2] and has evolved to include capabilities to measure viscoelastic properties of storage and loss moduli (E', E", tan δ).[3–7]

Bruker's FASTForce Volume CR brings enhanced contact resonance capability to Dimension® platform AFMs, enabling a faster, more accessible, easily implemented and robust means of nanomechanics measurement. In FASTForce Volume CR, the system scans an area on the sample surface, stopping to touch the surface at each pixel and sweep the frequency of mechanical excitation (see Figure 1a). The resonant frequency and shape of the contact resonance peak shifts in response to changes in the tip-sample properties, such as stiffness and dissipation, as shown in Figure 1b. Higher contact resonance frequencies correspond to stiffer materials while contact resonance peaks with a higher quality factor correspond to less dissipation or damping. In Figure 1b, this translates to material 2 having a higher stiffness and lower dissipation than material 1. Although originally developed to probe elastic properties such as stiffness,

the theory to interpret the dissipation through the shape of the peak (its quality factor) was developed over the past decade[4] opening up contact resonance as a technique to fully explore viscoelastic properties of materials. Until now, implementation of contact resonance has been hampered by its slow imaging speed, complex analysis, and specialized hardware for full-spectrum acquisition. FASTForce Volume CR has removed these hurdles through flexible, easy-to-use software based on widely-adopted and highly productive FASTForce Volume.

Figure 1. (a) Operating principle of FASTForce Volume CR; (b) The effect of material properties on contact resonance frequency and quality factor, showing material 2 has higher stiffness and lower dissipation than material 1.

Implementation of FASTForce Volume CR

In FASTForce Volume CR, the cantilever approaches the surface at each point in the image, then holds on the surface while the frequency is swept to collect the contact resonance tune, and then the cantilever is retracted. Figure 2 shows an example of the approach (blue), hold (green), and red (retract), where the top panel is force versus time, the middle panel is Z height versus time, and the bottom panel is a contact resonance tune. This real-time contact resonance tune shows three contact resonance eigenmodes at 310 kHz, 685 kHz, and 1.5 MHz on polypropylene. Note the flat baseline and excellent signal to noise on the peaks, indicative of a highly damped actuator with a well-coupled sample. Obtaining clean, background-free contact resonance tunes with a linear response to the drive is the first and most important step of contact resonance experiments, and is the key to a successful, quantitative measurement.

Figure 2. Schematic of implementation of FASTForce Volume CR. The blue panel shows the approach of the cantilever toward the surface, then a hold segment in green, and then retraction from the surface in the red panel. The bottom panel shows a sample contact resonance tune during the hold segment.

The advantages of this implementation are manifold. First, it sweeps the whole frequency range up to 5 MHz, enabling observation and tracking of multiple eigenmodes at once, as well as the detection of artifact peaks that should be ignored. The ability to survey all three modes simultaneously optimizes the measurement since the individual modes can be analyzed subsequently to select the one with the best discrimination and sensitivity. Depending on the material and cantilever, it is possible that only one contact resonance eigenmode would be present in this frequency range, in which case analysis would focus on that single mode.

By combining the contact resonance with force volume, this measurement also provides more information than just contact resonance allows alone. Both adhesion and a force-volume modulus measurement can be calculated at each point together with the viscoelastic moduli provided by contact resonance, providing a more complete understanding of the material properties at each point. Additionally, in contrast to other imaging-based contact resonance methods that are essentially contact mode, the force-volume-based method used in FASTForce Volume CR stops the XY scan during the tip-sample contact. This minimizes lateral forces on the tip, significantly reducing sample damage and tip wear. The combined contact resonance and force volume measurement provides a large amount of data, reflected in the large file sizes. For example, a "typical" image with 128x128 points is ~200 MB, depending on the length of time for each segment (approach/retract/hold) in the measurement. The software was specially designed to handle these large data files and provides convenient access to all the channels during real-time acquisition. This is coupled with integrated averaging and statistics in a streamlined GUI for subsequent analysis.

FASTForce Volume CR Operation

The operation of contact resonance has been streamlined with an emphasis on flexibility, ease of use, and convenient visualization and analysis of large data sets. The measurement is run through mechanical actuation of the sample in a technique referred to as atomic force acoustic microscopy (AFAM), and two sample transducers are provided to hold a sample and a reference in order to facilitate toggling between the two.

The operation of FASTForce Volume CR requires a few key additional parameters to a typical force ramp measurement, which are the hold time on the surface, the modulation amplitude (similar to a drive amplitude), and the start and end frequencies for the sweep. The hold time for the sweep has been traditionally the limiting step for contact resonance measurements, making them very slow. In FASTForce Volume CR, a typical hold time for an entire frequency sweep can be as low as 10 ms. In combination with the force-volume measurement, every pixel would

thus take ~20 ms to acquire. Acquisition can be sped up significantly by narrowing the frequency bandwidth to a sweep of a single mode, resulting in the collection of a 256x256 image in under 30 minutes. Minimal calibrations are required and consist of finding the resonant frequency and quality factor of the free air oscillation modes of the cantilever, which are conveniently populated into the image file for real-time or subsequent analysis. These calibrations are in addition to the standard spring constant and deflection sensitivity calibrations for all force volume measurements. All the required calibrations are accomplished through dedicated, step-by-step GUIs.

In addition to the conventional acquisition of the contact resonance frequency and quality factor, real-time acquisition is now possible of the amplitude, stiffness, and viscoelastic parameters of storage modulus, loss modulus, and loss tangent. These viscoelastic parameters are calculated in real-time or can be calculated later from the saved data. These channels are in addition to the parameters collected from the force-ramp, such as the force volume modulus and adhesion.

Figure 3 shows contact resonance tunes on the different components of a three-polymer blend of polyethylene (PE), polystyrene (PS), and polypropylene (PP). First a sweep of all the contact resonance peaks was done, showing the three eigenmodes at 296 kHz, 567 kHz, and 1.26 MHz (top panel). Frequency sweeps on the three materials easily differentiate between the three materials in the second mode, as shown in the bottom panel. The PS showed the highest frequency (i.e., the stiffest material) and the PE, the lowest frequency (i.e., the softest material).
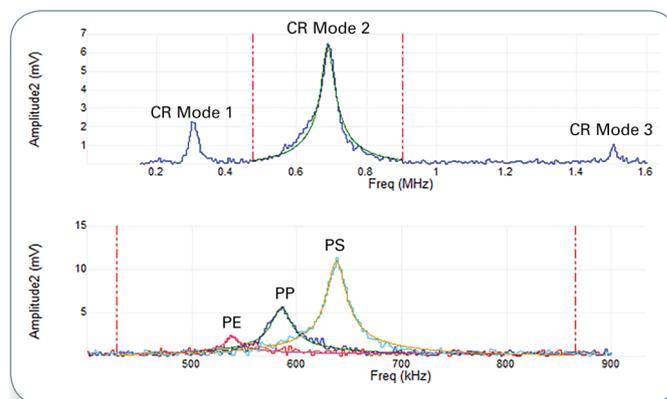
Figure 3. A sample contact resonance tune in the top panel revealing three contact resonance eigenmodes with a clean baseline. The contact resonance mode 2 is fitted to a Lorentzian to extract the appropriate frequency and quality factor parameters for further analysis. The bottom panel shows the second contact resonance mode on three different materials, easily revealing the difference in frequency and even the quality factor of the peak on these materials.

Figure 4 shows the images of topography, frequency, quality factor, and amplitude from real-time analysis of the second contact resonance mode. Any mode can be easily selected for these real-time calculations by simply re-positioning the red cursors around the desired mode. The Bernoulli beam model with tilt and modified with the Kelvin-Voigt model[8] is then applied to this data. A reference sample with known mechanical properties is necessary to generate calibration factors to analyze unknown samples, which in this case was the internal reference of polypropylene. If the sample has no known components, a second actuator is available to allow calibration using an appropriate reference sample. Once the system is calibrated, the software automatically makes the calculations and outputs quantitative maps of viscoelastic properties, including storage modulus (E') and loss modulus (E"), which are shown in Figure 4c and 4d.

From Polymers to Metals

Contact resonance can measure a wide variety of materials from polymers to metals. Below are a few examples of contact resonance measuring viscoelastic properties of a series of polymers with moduli in the range of a few GPa. There are also examples of contact resonance probing the elastic properties of significantly stiffer materials, such as semiconductors, metals, and complex inorganic films with moduli in excess of 100 GPa. With application to such a wide range of moduli and the ability to probe both elastic and viscoelastic properties, contact resonance is a powerful tool for nanomechanical measurements.

Probing viscoelastic properties: E' and E"

As previously discussed, the viscoelastic properties of three polymers (PE, PS, and PP) are mapped in Figure 4. In these maps, the three materials are differentiated by contrast, with the contact resonance amplitude showing the strongest differentiation among the components. The storage modulus map allows the PE to be easily distinguished from the PP and PS. In the loss modulus map, it is easy to discriminate between PP and PE or PS. A variety of models are provided to calculate the loss modulus, including ones that require a reference loss modulus[9,10] and a model that does not.[8]
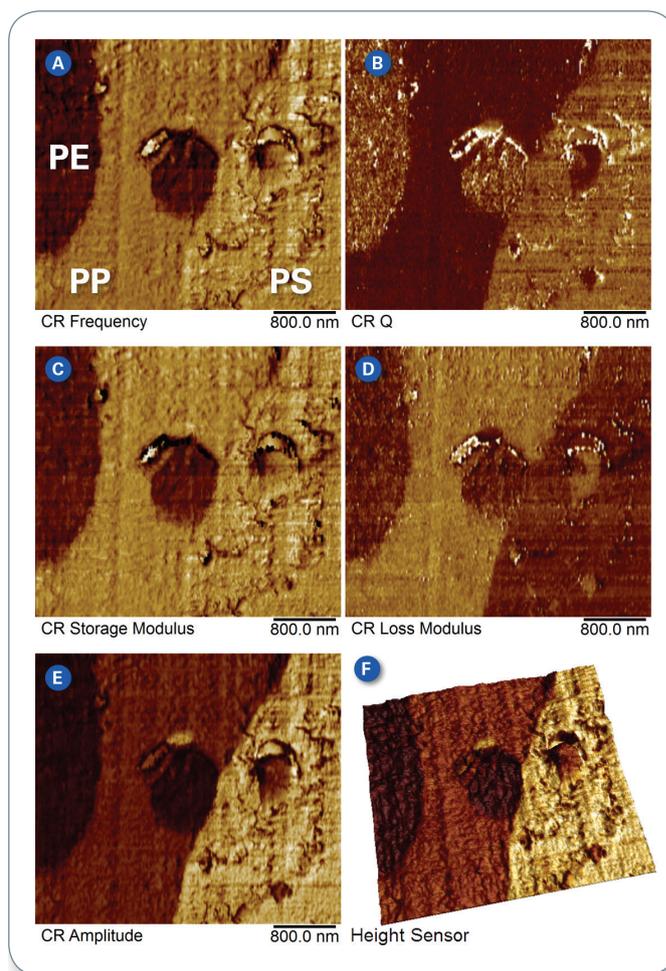
Figure 4. Various channels from the FASTForce Volume CR experiment: a) contact resonance frequency (dark-to-bright Z scale is 519.5 – 653.3 kHz); b) contact resonance quality factor (dark-to-bright Z scale is 1.572 to 23.3); c) storage modulus E' (dark-to-bright Z scale is 270.8 MPa to 4 GPa); d) loss modulus E" (dark-to-bright Z scale is -16.8 MPa to 374.2 MPa); e) contact resonance amplitude (dark-to-bright Z scale is -6.2 to 62.4 mV); and f) 3D rendering of topography with skin based on CR amplitude.

Table 1 provides a comparison between the viscoelastic moduli from the bulk measurement by dynamic mechanical analysis (DMA) with those measured by contact resonance for the maps in Figure 4. Note that DMA measurements have been time-temperature superposed to the frequency of the contact resonance measurement for proper comparison. Because in this sample the PP also serves as an internal reference, the ratio of the various moduli with respect to PP are also presented in the final two columns. For storage modulus (E') the trend of PS>PP>PE is the same with good agreement between the absolute storage modulus values. The loss modulus has been calculated by two different models described above, PKAS[8] and YHT[9]. For the loss modulus (E"), the trends are again the same between the two methods of PP>PE>PS but the absolute values differ greatly. Loss modulus measurements, which depend on an accurate determination of the peak shape and quality factor calculation, are generally less accurate than storage modulus measurements that rely primarily on the frequency peak position.[5]

Viscoelastic Moduli vs. Contact Resonance

	PP (GPa)	PS (GPa)	PE (GPa)	PS:PP	PE:PP
E' DMA	2.60	2.9	2.1	1.11	0.81
E' CR	2.63	2.79	1.5	1.06	0.57
E" DMA	0.126	0.029	0.062	0.23	0.49
E" CR (PKAS)	0.200	0.112	0.125	0.56	0.63
E" CR (YHT)	0.128	0.074	0.08	0.58	0.63

Table 1. Comparison between the viscoelastic moduli from the bulk measurement by DMA with those measured by contact resonance for the maps in Figure 4.

Figure 5 shows another example of contact resonance imaging of a polymer blend of polystyrene and polycaprolactone (PCL). Clean frequency sweeps on the sample show the three contact resonance modes for further analysis. In the top set of data, the second eigenmode is chosen for calculation of the storage and loss moduli, revealing strong discrimination between the PCL and PS materials in both channels. On the bottom set of data, a simple repositioning of the red cursors selects the third mode for analysis to generate maps of E' and E". This third mode is less sensitive to the material properties, and thus shows less contrast between the materials in both storage and loss modulus maps. The points that are filled in blue are those where the model did not fit the data and so those points are discounted in the analysis. Note also that there is no degradation of these soft polymers with the FASTForce Volume CR imaging.
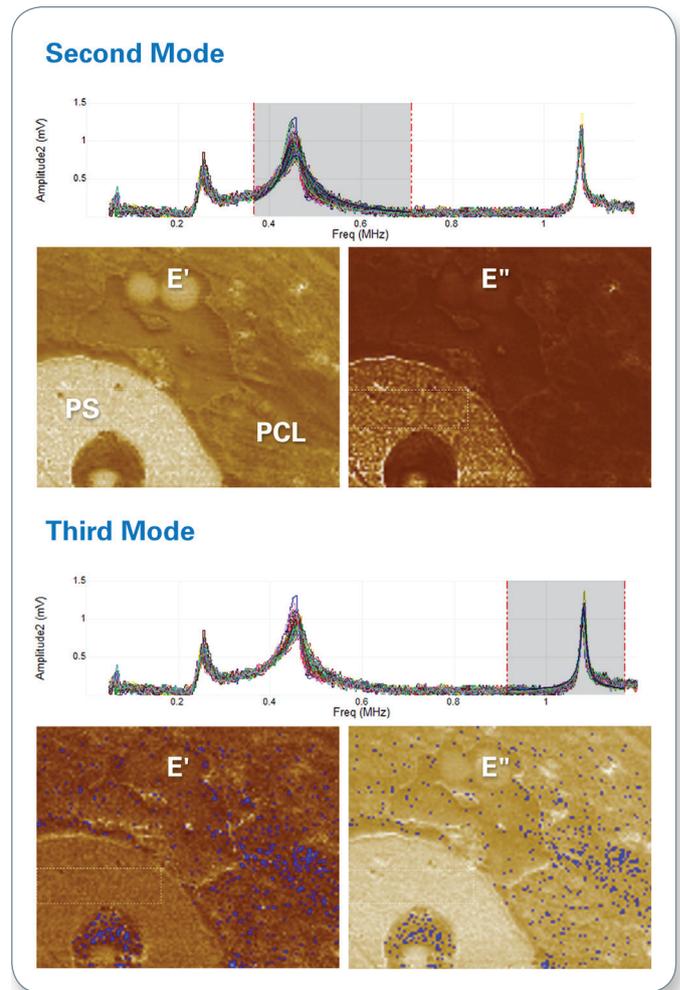
Figure 5. Contact resonance tunes and resulting E' and E" maps of a blend of PS-PCL: a) analysis of second eigenmode with corresponding E' map (dark-to-bright Z scale is -4.8 GPa to 4.8 GPa) and E" map (dark-to-bright Z scale is -200 MPa to 200 MPa); b) analysis of same image area but with the third contact resonance eigenmode and corresponding E' and E" maps, revealing poorer discrimination than second mode. Data acquired in collaboration with Prof. Philippe Leclére, U. Mons, Belgium.

Probing elastic properties of stiff materials

Contact resonance is also suitable for stiffer material with higher moduli; in fact the technique was originally invented to probe the mechanical properties of such materials with relatively soft AFM cantilevers. However, a serious challenge historically with this class of measurements was tip wear, which directly affects the tip-sample contact area and thus contact resonance frequency, which is a key parameter. This problem is circumvented here with the use of diamond-coated probes. A storage modulus map of a sample layered with aluminum, silicon, and chromium is shown in Figure 6. This sample spans a modulus range of tens of GPa to a couple of hundred GPa. The figure shows a series of modulus maps collected at different loads exerted on the surface from 200 nN on the left to 1000 nN on the right. The silicon component served as the internal reference for this sample.
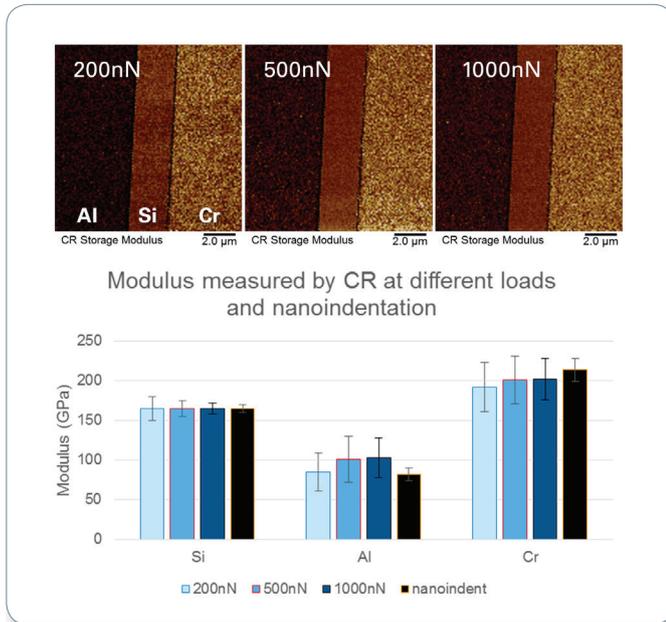
Figure 6. FASTForce Volume CR conducted on a sample composed of 50 nm films of aluminum and chromium on silicon at different loads. On the left is the storage modulus map imaged at 200 nN load (dark-to-bright Z scale of all images is 32.5 GPa to 320.5 GPa). In the middle is the E' map at 500 nN load and on the right is the E' map at 1000 nN load.

The modulus measurements of all three materials at the different loads are identical (within error) as shown in the bar graph comparing the measurements at different loads (see Figure 6). The error bars on the contact resonance measurements represent the standard deviation for the specific component within the image. The chart also includes for comparison nanoindentation measurements on the three components. The chromium modulus measured by contact resonance, approximately 200 GPa, is in good agreement with a modulus of 214 GPa from nanoindentation. The modulus of the aluminum, 85–103 GPa depending on the load, corresponds well with the 82 GPa measured by nanoindentation.

Figure 7 shows the same sample at the beginning (left) and end (right) of a series of 80 images (327,680 contact resonance spectra) collected on the identical area, showing no degradation in either topography or the measured modulus of the materials. Though previous implementations of contact resonance imaging suffered from tip wear due to contact mode imaging, FASTForce Volume CR coupled with diamond-coated probes significantly reduces the wear on the tip, enabling reliable and repeatable measurements even on very stiff materials.
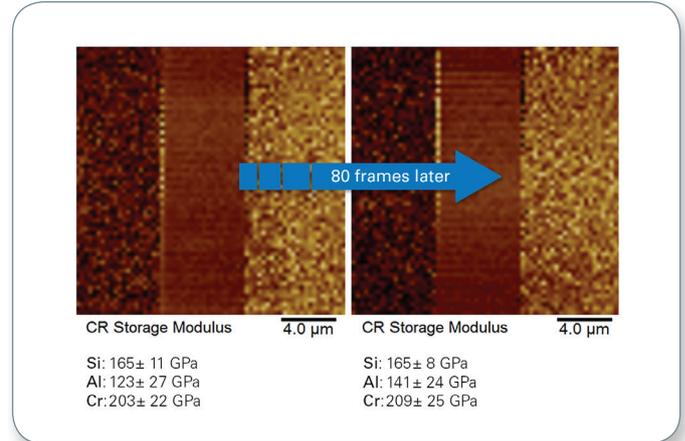
Figure 7. FASTForce Volume CR on a blend of aluminum, silicon, and chromium showing initial image (left) and the same area imaged 80 frames later (right) revealing no degradation in image quality or measurement stability.

Conclusion

FASTForce Volume CR has removed many of the hurdles associated with contact resonance by coupling the productivity of FASTForce Volume with flexible software. Large data volumes are handled with easy-to-use GUIs for straightforward analysis and interpretation. It quantitatively measures the modulus (through force-volume) and the viscoelastic properties of viscoelastic storage modulus (E'), loss modulus (E"), and loss tangent. By conducting the measurement through FastForce Volume, tip wear and sample damage are minimized while acquisition speed is maximized. FASTForce Volume CR offers a fast, accessible, and easy-to-use implementation of contact resonance for quantitative measurements of elastic and viscoelastic properties applicable to a range of materials, from polymers to metals.

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