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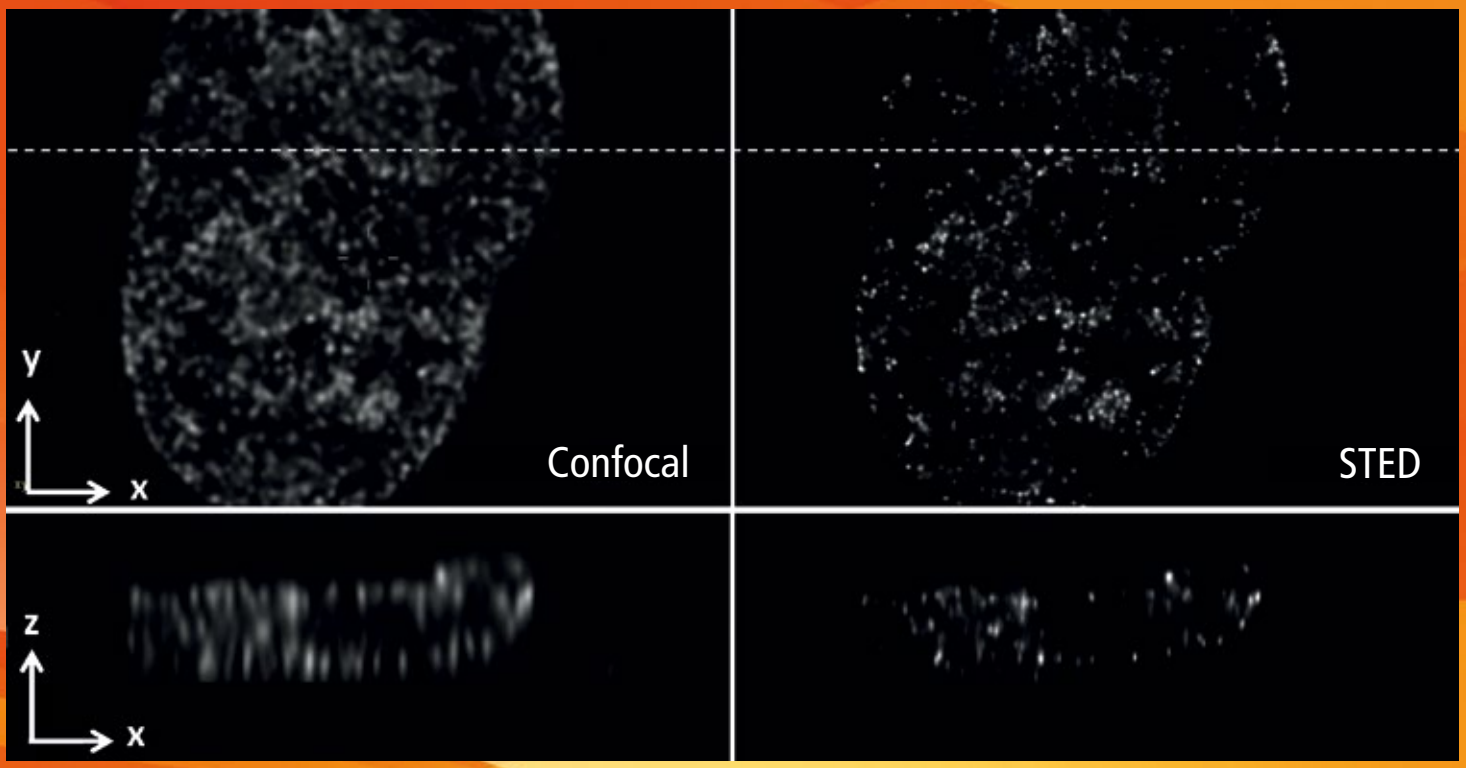

Bioluminescence Microscopy

Camera Technology

Contact Resonance Imaging

High-Resolution Electron Microscopy

Exploring Nanoscale Viscoelastic Properties

Recent Advances in Contact Resonance Imaging with AFM

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Development of advanced materials relies on a detailed understanding of nanoscale morphology and mechanical properties. Atomic Force Microscopy (AFM) has become a key tool in material science by providing this information. Contact Resonance imaging has emerged as a powerful AFM technique for its ability to quantitatively characterize the viscoelastic response of materials, its applicability to a wide range of materials, and its ability to provide this information quickly and at high resolution.

Origins of Contact Resonance Imaging

Contact resonance (CR) imaging arose from work in the 1990's by the Yamanaka and Arnold groups [1,2]. It is based on the principle that the contact resonant frequency and quality factor (Q) of an AFM cantilever changes in response to variations in the tip-sample stiffness and damping (fig. 1). The contact resonance is measured by introducing a very small vertical modulation to either the cantilever base, a method sometimes called Ultrasonic Force Microscopy (UFM), or to the sample, a method sometimes called Atomic Force Acoustic Microscopy (AFAM). In either case, the cantilever response can then be measured. Early versions operated at a single frequency and measured the amplitude response near the contact resonance. This can provide contrast that qualitatively depends on the tip-sample stiffness. However, since amplitude depends on both the elastic and dissipative interactions, the contrast is ambiguous. In fact, the image contrast can be inverted, depending on whether the response is measured above or below the contact resonance [3].

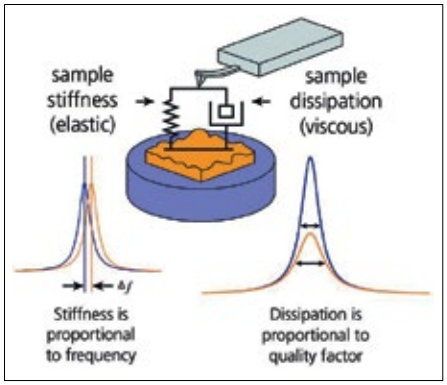

Fig. 1: Schematic of the tip-sample contact resonance model.

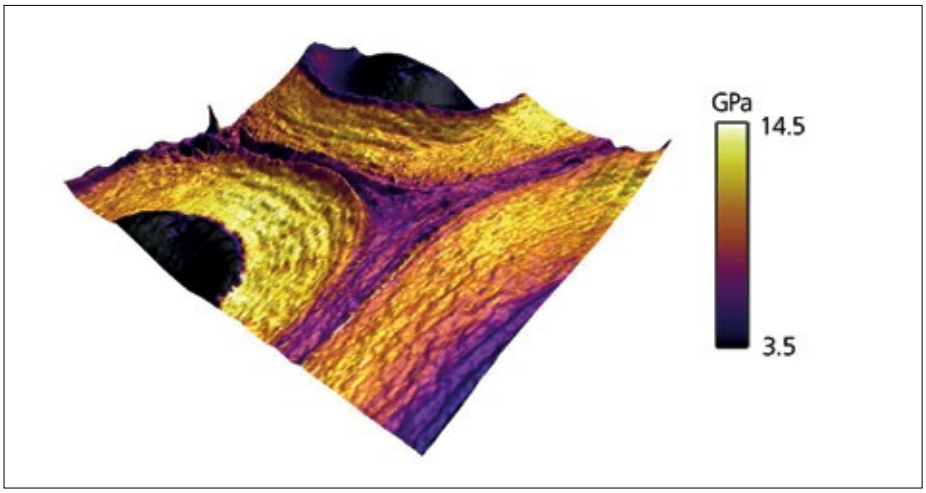

Fig. 2: CR elastic modulus map of Arabidopsis plant cell overlaid on 3D sample topography. 4 µm scan using custom SPRITE on an Asylum Research Cypher S AFM. Image courtesy of Jason Killgore (NIST). Sample courtesy of Bryon Donohoe (NREL).

The tip-sample stiffness can, however, be directly related to the contact resonance frequency. As the cantilever scans over the surface, changes in the resonance therefore map the localized stiffness. One way to directly track the resonance frequency is to use a "phase-locked loop" (PLL) [4]. Unfortunately, spurious phase shifts in the electronics, actuation and even the sample itself can lead to inconsistent results and poor tracking stability [5]. One solution that mitigates these errors is to measure a more complete spectrum by performing a frequency sweep around the resonance on a point-by-point basis. However, this method is inconveniently slow for practical image acquisition, typically requiring up to several seconds per pixel [3,4].

Faster, More Quantitative CR Imaging

Recent developments have increased the speed of CR imaging while also making it simpler and more quantitative. These improvements have focused not only on frequency tracking, but also on more fully quantifying the contact resonance, which is defined by at least three unknown variables: frequency, Q, and amplitude. Therefore single frequency techniques cannot measure enough observables to fully characterize it. One approach, taken by Hurley *et al.* [6], recognized that prior frequency sweep methods were limited in speed by instrumentation. Using a fast digital signal processor, their "Scanning Probe Resonance Image Tracking Electronics" (SPRITE) is able to measure the contact resonance at a rate of less than 3 ms per spectrum, typically averaging 3-4 spectra per pixel, for an effective rate of about 10 ms per pixel (fig. 2) [6]. Ultimately though, the speed of CR measurements is fundamentally limited by the frequency and Q of the cantilever, that is, how fast it can ring up or ring down at each frequency measured. For a spectra

with N frequencies measured, the minimum time per spectra is ~NQ/ω. This issue was noted by Jesse *et al.* [7], who found that it could be circumvented by using a mixed frequency signal to drive an entire frequency band at once (effectively reducing N to 1) and then recovering the CR spectra using Fourier analysis. Coined Band Excitation (BE), it can operate at speeds of about 1-4 ms per spectra, regardless of the frequency, Q, and width of the band sampled (fig. 3). Depending on averaging, this results in an effective rate of 1-10 ms per pixel. Though similar in speed for a nominal case where N=128, f=300 kHz and Q=50, the BE technique begins to outpace SPRITE in cases where the Q is higher, the frequency is lower, or a wide frequency band is measured. Notably, SPRITE and BE require specialized hardware that can transfer and analyze large amounts of data at high speed. Dual AC Resonance Tracking (DART) presents a novel solution to this problem. Whereas both SPRITE and BE characterize the full amplitude vs. frequency spectra within some range, DART instead monitors the amplitude and phase at just two frequencies bracketing the resonance [5]. By using the two amplitude signals in the frequency tracking feedback loop, the phase errors discussed above for PLL feedback are avoided. Furthermore, measuring the response at two frequencies provides enough information to not only track the resonance, but also to fully reconstruct the CR spectra assuming a simple harmonic oscillator response [8]. The technique is very fast and readily implemented using the lock-in amplifier electronics already present in commercial AFM controllers.

Measuring the Viscoelastic Response

Early CR work focused on measuring stiffness and elastic modulus. It wasn't until 2001 that the Q was mapped and associated with loss modulus [4]. Dissipation remained largely ignored until recently when the theory to fully interpret it was developed [9]. Now, the Q is widely measured and used to calculate loss modulus [8]. This capability to measure the full viscoelastic response has become more important as CR imaging has begun to be applied to polymeric materials (fig. 4) [10,11].

Making CR Imaging More Quantitative

CR imaging obtains quantitative nanomechanical properties by analyzing changes in frequency and Q. The contact frequency and contact Q are calculated from experimental data by fitting the damped simple harmonic oscillator model to the resonance spectrum at each pixel. Additionally, the vibrational mode, free resonant frequency, and free Q of the cantilever are measured. To extract elastic modulus (E') and loss modulus (E") of a sample, these experimental values must first be related to the normalized tip-sample contact stiffness and to the damping coefficient. This is done using the Bernoulli beam model modified with the Kelvin-Voigt model, details of which are explained in Killgore *et al.* [10]. Since CR imaging is a calibration-based approach, initial analysis of a

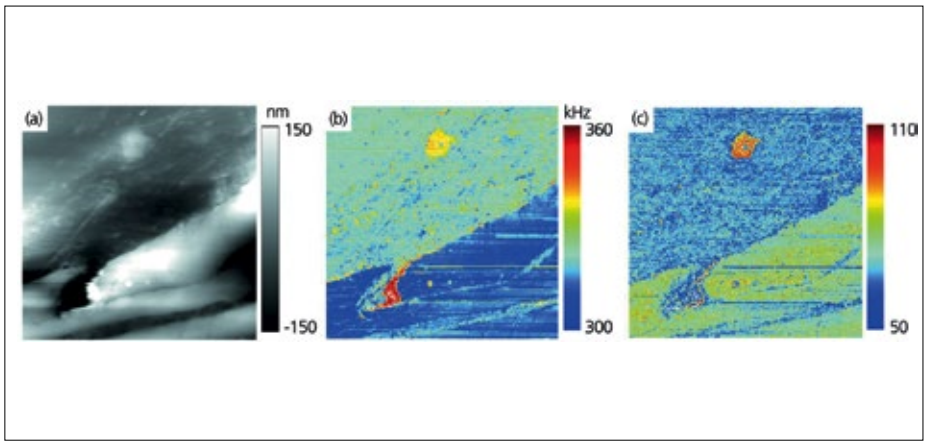

Fig. 3: CR images of subbituminous/bituminous coal (a) topography (b) frequency shift (c) quality factor. 15 µm scan using custom BE electronics on an Asylum Research MFP-3D AFM. The nanoscale structure of coal is highly inhomogeneous and its properties have important implications for mining and energy utilization. Image courtesy of Sergei Kalinin, Liam Collins, and Stephen Jesse (ORNL).

reference sample with known mechanical properties is required before analyzing unknown samples.

Commercially, these steps are automated on Asylum Research AFMs with Contact Resonance Viscoelastic Mapping Mode. One simply acquires an image of a reference sample, and then enters its elastic and loss moduli, along with the probe parameters into the software interface. The software automatically calculates the required factors and returns the calibration values. Finally, the unknown sample is scanned and these calibrations are used to generate the E' and E" images. This interface makes quantification of CR data quick, simple and reproducible without requiring a detailed understanding of the analysis calculations.

Recent Applications of CR Applications

One advantage of CR imaging is that it can provide quantitative nanomechanical information from extremely small material volumes. In the semiconductor industry nanoindentation has been commonly used to assess the mechanical properties of materials, but shrinking feature sizes are making those measurements more difficult. For instance, the thickness of low-k dielectric layers can be <100 nm. Stan *et al.* have recently shown that CR imaging allows for quantitative characterization of copper interconnects and low-k dielectrics. Interestingly, the elastic modulus of patterned low-k dielectric materials were twice as high as pristine films [12].

The ability of CR imaging to measure both elastic and viscous properties has also made it a powerful tool for composite materials. The strength and stiffness of the interface between components affects overall the strength of the composite. Zhou *et al.* have used DART CR imaging to study glass fiber reinforced polymer composites and compared their findings with nanoindentation data [13,14]. They found that the moduli values agreed between the two techniques and relative errors were smaller with CR measurements. Furthermore, CR imaging allowed for the direct characterization of the interface width (~500 nm) as well as the stiffness variation along this transition zone at length scales not accessible to nanoindentation (fig. 5).

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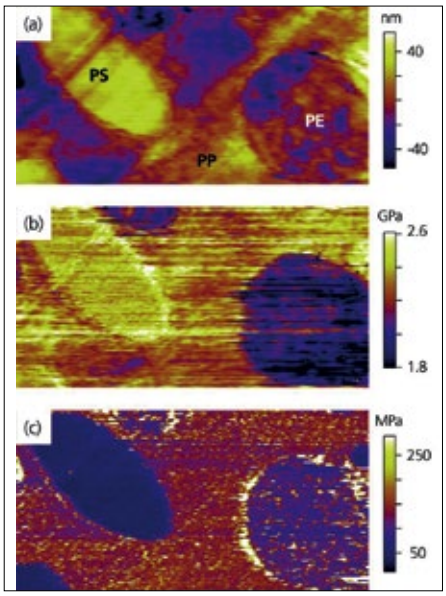

Fig. 4: CR images of PP/PE/PS polymer blend (a) topography (b) elastic modulus (c) loss modulus. 5x10 µm scan using DART-CR on an Asylum Research MFP-3D AFM. Note the very different contrast in elastic and loss modulus, where the E' for PS and PP are very similar and much higher than PE, but the E" for PS is much lower than both PP and PE. Figure adapted from [11].

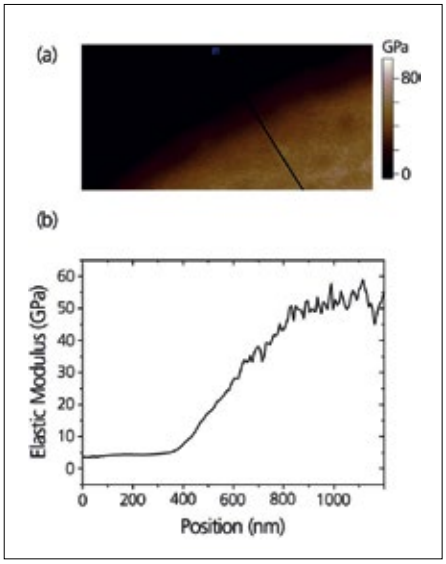

Fig. 5: CR images of a glass fiber polymer composite (a) elastic modulus (b) modulus profile along the line shown in (a). 1x2 µm image using DART-CR on an Asylum Research MFP-3D AFM. The profile shows a clear transition region ~500 nm in width between the glass and polymer. Figure adapted from [13], courtesy of Prof. Faxin Li, Peking University, China.

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