Nanoscale subsurface imaging via resonant difference-frequency atomic force ultrasonic microscopy

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A novel scanning probe microscope methodology has been developed that employs an ultrasonic wave launched from the bottom of a sample while the cantilever of an atomic force microscope, driven at a frequency differing from the ultrasonic frequency by the fundamental resonance frequency of the cantilever, engages the sample top surface. The nonlinear mixing of the oscillating cantilever and the ultrasonic wave in the region defined by the cantilever tip-sample surface interaction force generates difference-frequency oscillations at the cantilever fundamental resonance. The resonance-enhanced difference-frequency signals are used to create images of embedded nanoscale features.

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The rapid development of new materials produced by the embedding of nanostructural constituents into matrix materials has placed increased demands on the development of new measurement methods and techniques to assess the microstructure-physical property relationships resulting from such embedding. Although a number of techniques are available for surface characterization, methods to assess subsurface structures at the nanoscale remain largely in development. Several successful efforts at nanoscale subsurface imaging have involved combining the lateral resolution of the atomic force microscope[1] (AFM) with the nondestructive capability of acoustical methodologies for assessing subsurface features of materials[2-11]. The utilization of the AFM in principle provides the necessary lateral resolution for obtaining subsurface images at the nanoscale. The use of acoustic waves in the ultrasonic range of frequencies more optimally takes advantage of this resolution, since both the intensity and the phase variation of waves scattered from nanoscale features increase with increasing frequency[12]. A basic problem with probing at ultrasonic frequencies, however, is the reduced response of the AFM cantilever.

To avoid the reduced cantilever response at ultrasonic frequencies, we have developed a new methodology utilizing difference-frequency signals that requires only the addition of off-the-shelf peripheral instrumentation for implementation and does not require modification to any part of the AFM, in contrast to the recently reported difference-frequency technique of Shekhawat and Dravid[11]. The new technique, called resonant difference-frequency atomic force ultrasonic microscopy (RDF-AFUM), utilizes the fundamental and harmonic resonances of the AFM cantilever for the cantilever drive signal as well as for the difference-frequency signal resulting from the mixing at the sample top surface of the cantilever drive signal and ultrasonic wave propagating from the bottom of the specimen. In this methodology, the cantilever, typically driven between the fifth and ninth overtones of the cantilever, engages the sample surface while a bulk ultrasonic wave, differing from the cantilever drive frequency by the fundamental resonance frequency of the cantilever, is launched from the bottom of the sample. The nonlinear interaction of the cantilever and the bulk wave in the region defined by the cantilever tip-sample surface interaction force gives rise to cantilever oscillations characterized by a resonant difference-frequency. Variations in the amplitude and phase of the bulk wave due to the presence of subsurface nanostructures affect the amplitude and phase of the difference-frequency signal. These variations are used to create spatial mappings of subsurface nanostructures.

A schematic of the RDF-AFUM equipment arrangement is shown in Fig.1. A Veeco Instruments Nanoscope IV MultiMode AFM is used for control and processing of the images. The drive signal to the AFM cantilever, operating in TappingMode at a suitable harmonic of the cantilever fundamental resonance frequency, is sent from the AFM control box to a broad-band piezo-stack under the cantilever. An HP model 3325A function generator is used to deliver a sinusoidal driving signal to a 2.0 MHz narrow-band PZT transducer bonded to the surface of the sample opposite the cantilever. The cantilever drive and transducer drive signals are split and fed to a mixer. The mixer output signal, consisting of sum and difference frequency signals, is sent to the reference input of a PAR model 5302 lock-in amplifier that, because of its limited bandpass, filters out the sum frequency. The AFM photo-diode signal, derived from the cantilever response from all sources, is then sent to the signal input of the lock-in amplifier where all frequencies except the difference-frequency are filtered out. The lock-in amplifier measures both the amplitude and phase of the input difference-frequency signal. The appropriate output signal from the lock-in amplifier is fed to the AFM processor to build up either an amplitude or phase image as the sample is scanned.

Before commencing a scan, it is useful to determine the set-point value of the feedback parameter that maximizes the amplitude of the difference-frequency signal. The TappingMode may be operated while holding one of three parameters constant in the AFM feedback loop: (1) the quiescent deflection of the cantilever, (2) the amplitude of the cantilever's response to the piezo-drive signal ("normal" amplitude), and (3) the phase lag between the cantilever's response to the piezo-drive signal and the drive signal itself ("normal" phase). Calibration curves are taken in which the values of each of these possible feedback parameters are plotted together with the difference-frequency amplitude as functions of position as the cantilever is ramped into and withdrawn from the sample surface. From these curves a feedback parameter and a set-point value are chosen to coincide with the maximum difference-frequency signal. Generally, the "normal" amplitude produces the most stable difference-frequency signal when used as the feedback parameter.

As the cantilever tip engages the sample surface, it encounters an interaction force that varies with the tip-surface separation distance. The deflection of the cantilever obtained in calibration plots is related to this force. For small slopes of the deflection versus separation distance, the interaction force and cantilever deflection curves are approximately related via a constant of proportionality. Figure 2 shows a comparison of the cantilever deflection (Fig. 2a) and the amplitude of the difference-frequency signal

(Fig. 2b) plotted as functions of the tip-surface separation. The maximum difference-frequency signal amplitude occurs when the quiescent deflection of the cantilever approaches the bottom of the force well, where the maximum change in the slope of the force versus separation curve (hence maximum interaction force nonlinearity) occurs. The exaggerated decrease in the cantilever deflection at the bottom of the force-separation curve (Fig. 2a) results from moisture accumulation on the cantilever tip and sample surface. During scanning, however, the effects of moisture are minimized and the cantilever deflection-separation curve becomes "smoother" near the bottom of the well.

A specimen consisting of a monolayer of gold particles, roughly 15 nm in diameter and embedded within a polymeric matrix roughly 20 μm beneath the sample surface, was imaged using both AFM and RDF-AFUM. The images are shown in Fig. 3. A conventional TappingMode AFM image of surface topography is given in Fig. 3b. An RDF-AFUM phase image is shown in Fig. 3c. Local surface variations of the elastic modulus and mass density of the polymer as well as surface topography contribute to the phase of the RDF-AFUM signal and result in the large scale features observed in Fig. 3c. More importantly, unique circular features appear in the RDF-AFUM phase image that are roughly 10-15 nm in diameter and do not appear in the AFM image. Fig. 3d is a line-scan from the central region of the micrographs (as indicated by the line in Fig. 3c) giving the phase variation of the RDF-AFUM signal plotted as a function of cantilever tip position on the sample surface. The region between the arrows in Figs. 3c and 3d shows the effects of a gold particle roughly 12 nm in diameter. The magnitude of the phase variations obtained between the arrows is roughly two to three degrees and is of a magnitude that would be expected in the RDF-AFUM mode from acoustic scattering from Au particles of this size. The circular object indicated in the upper right quadrant of Fig. 3c is thought to occur from a gas-filled void, since the image contrast is reversed from that of the gold particles. Such contrast reversal results from a phase lag generated by the gaseous void relative to the stiffer polymer matrix material as opposed to a phase advance generated by the gold particle having an even larger elastic modulus.

The above results provide clear evidence that RDF-AFUM can be used to obtain images of nanoscale subsurface features without the need to make any modifications to the AFM itself. The technique requires only the addition of off-the-shelf instrumentation for implementation and takes advantage of ultrasonic-range probing signals propagating through the bulk of the sample. A more complete understanding of the nonlinear interactions responsible for the generation of the difference-frequency signals and the resulting image contrast would be helpful in the interpretation and more quantitative exploitation of RDF-AFUM micrographs. A comprehensive analytical model of cantilever dynamics in the nonlinear interaction region is presently in development for such purposes.

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FOOTNOTES AND REFERENCES

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FIGURE CAPTIONS

Fig. 1. Schematic of equipment arrangement for the resonant difference-frequency atomic force ultrasonic microscope (RDF-AFUM).

Fig. 2. Calibration plots taken as the cantilever is extended over a distance of 200 nm: (a) cantilever deflection curve; (b) difference-frequency signal. Maximum difference-frequency signal occurs near bottom of force well.

Fig. 3. Results obtained from sample consisting of a monolayer of gold particles (10-15 nm in diameter) roughly 20 μm beneath the sample surface: (a) Depiction of specimen; (b) AFM TappingMode image of surface topography; (c) RDF-AFUM phase image showing relatively large-scale features resulting from variations in surface physical properties and topography as well as small-scale circular features from the Au monolayer; (d) Line scan of phase signal versus position across center of micrographs [indicated by solid line in (c)]. The arrows frame a 15 nm diameter Au particle.

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Fig.1

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Fig. 2

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Fig. 3