All-optic UHV Atomic Force Microscopy.

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Abstract

Non-contact mode Atomic Force Microscopy is a very useful tool for precise measurement and mapping of the tip-sample interaction force. In the laboratory, several works were focused on the use of all-optic UHV AFMs for atomic resolution imaging with high frequency (1-200 MHz) and low amplitude of drive (10-100 pm). We recently implemented a new all-optic AFM for the measurement of gradient of frequency shifts and as a new tool for the development of innovative chemical contrast techniques. Two all-optic AFMs were also implemented into a Transmission Electron Microscope (TEM) and a Field Ion Microscope (FIM) for new applications in the field of surface chemistry. All the technical aspects covering high resolution imaging with all-optic AFM will be discussed in the former part of this review and their new implementations for gradient of frequency shift measurement in the latter.

1. Introduction

During the past decades, non-contact mode in atomic force microscopy (nc-AFM) has become a very accurate technique for measurement and mapping of the tip-sample interaction forces with atomic resolution. But determining the exact chemical composition on surfaces or nanostructures remains a difficult challenge. Dynamic atomic force microscopy still remains the method of choice to achieve controlled and reproducible chemical identification of individual atoms. A well-known milestone in this field is the "name that atom" study performed in 2007 by Y. Sugimoto et al. In their work, they showed that the value of the local minimum in force curves can provide intrinsic signatures for the identification of Si, Pb, and Sn atoms on a Si(111) surface. This technique can potentially image insulators, semiconductors and any other metal surfaces with true atomic resolution. It is after this work that some studies started to focus on the use of the gradient of frequency shift as a tool for chemical contrast. Towards true chemical contrast, the same group implemented a faster imaging technique by applying a small tip-sample distance dither around the frequency shift working-point, and used a lock-in amplifier to detect the amplitude and the sign of the modulated frequency shift. The lock-in amplifier output was mapped in x and y to represent a qualitative chemical contrast. However, since the choice of the working frequency shift is arbitrary, it is difficult to guaranty a real chemical fingerprint characterizing each atom intrinsically. A recent work from Kawai et al. involved the use of eleven lock-in amplifiers for the dynamic detection of all the harmonics of the frequency shift curves allowing their full reconstruction on-the-fly. In our laboratory we also implemented some new detection techniques using measurement of the gradient of frequency shifts.

2. Optical excitation and detection

During the past few years, the laboratory has published series of works concerning implementation of all-optic AFMs. All the AFMs developed in our laboratory use cantilever detection by heterodyne laser Doppler interferometry. The photothermal excitation was chosen for its extremely clean excitation even at low amplitude (10 pm) and high frequency (100 MHz). The detection scheme involves the use of a superheterodyne circuit working at an intermediate frequency of 10.7 MHz, with the specificity to use directly the velocity signal for the self-excitation feedback loop. For the studies presented herein, we used two types of laser diodes (Neoark) with optical wavelengths of 405 and 780 nm and having an average incident light power.
of 2 and 4 mW, respectively. The laser-diode beams were introduced into the same optical path of the optical microscope and were incident on the rear surface of the cantilever through an objective lens. The light power of the excitation beam transmitted through the cantilever was measured using an optical power meter placed on the side opposite to the objective lens. Cantilever deflection velocity was measured using a laser Doppler interferometer with a carrier frequency of 80 MHz, whose light source was a frequency-stabilized helium-neon laser, with a source output power of 2 mW. The actual incident power on the cantilever was only 0.6 mW and the positions of the excitation and detection laser spots were adjusted by observing the optical image of the cantilever obtained using a CCD camera. Fundamental, second, or third mode of flexural, or torsional, could be confirmed by scanning a small laser spot with a diameter of 1.2 μm on the backside of the cantilever. The resonance peaks were identified with a network analyzer.

This all-optic set-up offers also the possibility to add one more excitation laser for multimodal excitations. Such modification of the system can allow selective detection of short-range interaction forces and acquisition of more details of the force curves in real-time for 3D force gradient mapping.

### 3. Imaging with atomic resolution

Piezo excitation experiments were carried out with conventional cantilevers operating at their fundamental and higher modes, as well as home-made short and stiff cantilevers with high resonance frequency for high resolution imaging. Using amplitudes of drive below 100 pm, imaging of metastable surfaces of quenched Si(111), as well as single atom manipulation at room temperature could be achieved. Figure 1 shows equifrequency shift mappings of Si (111) 7x7 structures taken with different amplitudes of drive. The acquired images were atomically resolved even with amplitude less than 0.3 Å. Surface of graphite, commonly known to be difficult to be observed under AFM due to its low level of force corrugation, could be correctly imaged with the same technique. Real-time imaging of AFM and STM gave new understanding of the overall contrast mechanism, the origin of giant corrugations, and the specific contrast mechanism of AFM on graphite. Figure 2 shows constant frequency shift images of GaAs (001)-c(8x2) with functionalized tips. Figure 2a was first recorded with a new clean Si tip. Figure 2b was recorded on the same area of the sample after the tip was intentionally brought into contact with the sample surface in order to change the nature of the tip apex. In both images, the specific orientation of c(8x2) reconstruction was observed but with completely different contrasts.

For the lateral mode, imaging using the torsional mode of the cantilever was just a matter of selecting the operating frequency to match the right natural frequency of the cantilever. Although not the entire field of view, typical features corresponding to the structure of Si(111)-(7x7) could be resolved. Using tunneling current for gap control with an amplitude of drive from 10 to 100 pm, lateral force gradient could be clearly resolved at the atomic level. The artifact’s effects between the crosstalks of lateral and vertical vibrations were subsequently confirmed with first principle calculations and simulations.

Photothermal excitation proved to be effective in a wide range of frequency from DC to 100 MHz. The photothermal excitation was also particularly useful for imaging samples in liquid environments. This technique offers the capability of imaging without perturbing the liquid environment due to piezo vibrations. Structure of mica in liquid could be imaged in lateral mode with an exceedingly better resolution than in vacuum. Membrane protein with atomic resolution could be resolved as well as pair functions measurements.
4. Gradient of frequency shift measurements

From these previous technological improvements, we recently implemented a new detection scheme for real-time acquisition of gradient of frequency shifts as a tool for new developments of chemical contrast imaging techniques. Figure 3 is a picture of this new all-optic AFM set up. In our new detection scheme, the centre of vibration of the cantilever is modified by adding a sinusoidal dither signal (dz) set at a given frequency (F_{dither}). The signal is generated from a signal generator and added to the z feedback signal controlling the tip-sample position. The cyclic change of the frequency shift (∆f) resulting from the dither motion is input to a lock-in amplifier, while the dither is set as the reference signal, to finally obtain the gradient of frequency shift (dΔf). Figure 4 represents the simplified block diagram of the set-up circuitry. F_{dither} must be set higher than the cut-off frequency of our home-made PI controller 19) in order to prevent any interference with the feedback loop during imaging.

As expected, it has also been demonstrated experimentally that large amplitudes of drive decrease the gradient of frequency shift noise. However, there is a trade-off between small amplitudes of drive, which give a better computation of the local derivative, and large amplitudes of drive that lessen the noise. We assumed that the noise level of the frequency shift is the same at the local minimum as the one at infinity.

During the simultaneous acquisition of ∆f and its derivative, clean signal could be obtained using a dither frequency up to 1 kHz. Figure 5 and 6 illustrate real-time detections of ∆f and its gradient using the lock-in amplifier during force curve acquisitions on KBr(001) with a dither frequency of 1 kHz. Dither amplitude was 2 Å and self excitation amplitude was set at 4 Å. The excursion frequency along the Z axis was 0.5 Hz (approach and retraction) for an excursion range of 4 nm.

5. FM demodulation using reciprocal frequency counter

The FM demodulator has recently been replaced with a home-made reciprocal frequency counter for better detection...
capabilities at higher frequency of dithers. Instead of regular frequency counters that count the number of oscillations of the input signal in a given time-frame, this new system measures the oscillation period of the input signal by counting how many pulses come from an extremely-high frequency clock source during one oscillation period. This method is a real-time FM demodulation since it produces a frequency for every single oscillation (counter clock demodulator). Figure 7 depicts the set of waveforms acquired with our new FM reciprocal demodulator. The vertical scale is 10 Hz/div. Δf is dynamically updated for each input pulse. The demodulator was designed for the 100 kHz-centered intermediate frequency of our newly designed superheterodyne cantilever oscillation circuitry. The reason why this rather low intermediate frequency was selected is that the frequency resolution of this method is inversely proportional to the square of the frequency itself, making low frequency more advantageous. The theoretical frequency resolution for 100 kHz signal is about 0.13 Hz per oscillation cycle.

With this new demodulator, cleaner frequency shifts could be obtained than with the previous crystal-based demodulator and for a range of frequency up to 10 kHz. As an illustration of this improvement, Figure 8 depicts the measurement of the frequency noise level (in RMS) at a bandwidth of 5 kHz for the overall detection system before and after our FM demodulator modification.

As a testing experiment, clean first harmonic (1ω) and second harmonic (2ω) of the frequency shifts could be measured on Si(111) in real-time and using a second lock-in amplifier operating at a frequency of 2Fdither up to 10 kHz. An example of such acquisition is depicted in Figure 9.

6. Gradient of frequency shift for new detection methods

For a better preparation of the sample right before being imaged, a new piezo scanner system containing its own joule heater has recently been installed in the main chamber of our AFM. Calibrations of the tube piezo were first performed under STM on Si(111)-(7x7) surface and clean atomic reconstruction could be observed. Good atomic resolution could be achieved in AFM mode while measuring the dΔf mapping with a dither of 1 kHz and an amplitude of 3 Å.

After these series of imaging experiments and calibrations, the gradient of frequency shift could be used as a tool for the development of two new chemical contrast mapping techniques. Both the techniques use a new type of feedback control using dΔf as an input value. Atomic resolution as well as chemical
contrast could be demonstrated. Details concerning these recent results are discussed elsewhere.\textsuperscript{29}

In parallel to the development of this technique, we combined our simultaneous detection of the frequency shift and its gradient with other atomic resolution microscopes. We could achieve successful measurements of frequency shifts and force curves inside a TEM that can routinely achieve atomic resolution using picometer-sized electron wavelength. Figure 10 represents a picture of an AFM tip under TEM during force curve and friction measurements. 3D nano-objects could be characterized using this combined TEM-AFM. Our laboratory also studies the combination of an AFM with a FIM. The FIM is an apparatus that allows the direct observation of individual atoms. We use this microscope to visualize vibration of organic molecules such as alkanethiols.

7. Summary

New types of all-optic AFMs were implemented and the combination of laser Doppler with photothermal excitation was a successful approach for high frequency at vibration modes up to 100 MHz and small amplitude of drive with various control schemes. A new all-optic AFM system allowing detection of the gradient of frequency shifts was also implemented. The scanner and real-time detection system offer clean atomic resolution capabilities. After the recent upgrades of our new home-made demodulator and on-the-fly detection scheme, two new strategies of imaging and chemical contrast could recently be investigated. All the theoretical aspects covering the experimental results of these new techniques are currently under submission. These new detection schemes can pave the way to new chemical contrast techniques allowing better contrast between different chemical species of atoms compared to other conventional techniques using the frequency shift as an input signal. These methods of detection have also been implemented inside a TEM and a FIM.

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