QUANTITATIVE MEASUREMENT OF ELASTIC CONSTANTS OF ANISOTROPIC MATERIALS BY ATOMIC FORCE ACOUSTIC MICROSCOPY

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Abstract: In Atomic Force Acoustic Microscopy (AFAM) the cantilever is vibrating in one of its resonance frequencies while the sensor tip remains in contact with the sample surface. The elastic constant which enters in the contact stiffness is the indentation modulus. The contact radius depends on the applied static force, the tip radius, and the elastic constants of the tip and the surface. It ranges between several and up to some tens of nm. Polycrystalline materials which appear elastically isotropic on a macroscopic scale are therefore anisotropic on the scale which is probed by AFAM. When ferroelectric ceramics are imaged, the acoustic images reveal the domains within the grains due to variations in contact stiffness. Furthermore, measurements on thin nanocrystalline films of piezoelectric ceramics have been performed revealing their piezoactivity as a function of annealing temperature are discussed.

Introduction: In Atomic Force Microscopy (AFM) [1] high-resolution images of sample surfaces are obtained by exploiting the deflection and torsion of micro-fabricated elastic beams with a sensor tip, which is in contact with the sample. AFM has found wide applications in diverse research fields, such as biology, physics and material science. Most AFM operation modes measure the deflection of the cantilever caused by the forces acting between the tip and the sample vertical to the sample surface while it is scanned. This allows mapping of surface properties such as topography, elasticity, magnetic or piezoelectric domains and various other quantities with nm resolution. However, in general both lateral and vertical forces contribute to the total tip-sample interaction. In dynamic AFM methods, the cantilever is vibrated while the sample surface is scanned. At least during a fraction of a vibration cycle the tip is in force contact with the sample. As imaging quantities the amplitude and the phase of the cantilever vibration, the change in the mean cantilever deflection and the contact resonance frequencies can be used. Techniques allowing topography measurements are e.g. the contact and the tapping mode [2]. With other operation modes additional sample surface properties can be imaged, like e.g. friction (Friction Force Microscopy) [3], elasticity (Force Modulation, Pulsed Force Mode, Ultrasonic Force Microscopy) [4-6], and magnetic (Magnetic Force Microscopy) [7] and ferroelectric domains (piezo-mode techniques) [8].

Experimental Technique: In the AFAM technique an AFM cantilever is set into flexural oscillations either by out-of-plane movements of the sample [9] caused by ultrasonic waves or by exciting the chip of the cantilever [10]. The oscillations are detected by the standard optical beam-deflection scheme of an AFM. Since the resonance frequency in contact depends on the contact stiffness between the tip and the sample surface, variations of the elastic properties of the sample lead to a shift of the resonance frequency. This shift can be used either in the spectroscopic mode in order to measure the local contact stiffness or to image variation in elastic properties [9, 10, 11]. In the AFAM imaging-mode one works at a fixed frequency near the cantilever contact-resonance. A shift of the resonance frequency leads to a variation of the oscillation amplitude allowing one to image qualitatively local variations of elastic properties. Originally, the AFAM technique was only operated with the bending modes of the cantilever, which means that tip and sample vibrations are mainly perpendicular to the surface. Further, experiments were carried out to excite torsional resonance by insonifying ultrasonic shear waves into the samples leading to an in-plane sample surface displacement. This offers the possibility to gain information on shear elasticity or frictional properties [12, 13].

In the piezo-mode [8], local sample surface vibrations are excited via the inverse piezoelectric effect by an ac-voltage applied to the sensor tip and a counter-electrode. Thus, the local piezoelectric activity of the sample determines the resulting cantilever vibration. In the ultrasonic piezo-mode, frequencies close to a contact resonance of the AFM cantilever are used to enhance the vibration amplitude by the Q-factor of the resonance and thus the image contrast [14, 15].

To render possible a quantitative evaluation of AFAM and ultrasonic piezo-mode images, it is convenient to use rectangular shaped cantilever beams, because their flexural and torsional vibration modes can easily be calculated. The cantilevers are described as elastic beams clamped at one end and with the sensor tip at the other end. Their free flexural and torsional resonance frequencies depend on its geometrical data and material parameters. A contact of the sensor tip with a sample surface stiffens the system and the resonance frequencies increase [9-18].

Data Evaluation: In general, vertical and lateral forces act in the tip-sample contact, which may contain elastic, adhesive, electric and magnetic parts, damping, and friction forces. If sufficiently large static loads F_c are applied to the cantilever which presses the sensor tip into the sample, the repulsive region of the force distance curve determines the interaction between tip and sample, and hence adhesion forces can be neglected. For an out-of-plane excitation vertical and for an in-plane excitation lateral elastic forces prevail and cause flexural and torsional cantilever vibrations, respectively. From the measured flexural and torsional contact-resonance frequencies the vertical and lateral stiffness of the contact k* and k^*_{lat} can be calculated [14-18]. For the analysis of lateral vibrations one has to take into account the tip length [11] and its lateral stiffness [18]. The Hertzian model of elastic contacts [19] relates the contact stiffness to the contact parameters:

$$k^* = \sqrt[3]{6E^*RF_c}\ , \qquad (1)$$

$$k^*_{lat} = 8a_cG^*, \qquad (2)$$

$$a_c = \sqrt[3]{\frac{3RF_c}{4E^*}}\ . \qquad (3)$$

Here, R is the tip radius, a_c is the radius of the contact area, and E* and G* are the reduced Young's and shear modulus of the contact, respectively. They depend on the Young's and shear moduli and the Poisson ratios E_t, E_s, G_t, G_s, ν_t, and ν_t of the tip and the sample:

$$\frac{1}{E^*} = \frac{1-\nu_t^2}{E_t} + \frac{1-\nu_s^2}{E_s}\ , \qquad (4)$$

$$\frac{1}{G^*} = \frac{2-\nu_t}{G_t} + \frac{2-\nu_s}{G_s}\ . \qquad (5)$$

Using the measured contact stiffness k* as input data, Eqs. (1) to (5) allow one to determine the local Young's and shear modulus of the sample surface if the geometrical data and material parameters of the cantilever and sensor tip are known. The quantitative contact resonance spectroscopy is similar to nanoindentation measurements albeit at lower loads and with a higher resolution.

The cantilever data provided by the manufacturers are sources of inaccuracies and errors in the experiments. Normally, the shape of the cantilever deviates from a rectangular beam of constant cross section changing its vibration spectrum. A further problem is mode-coupling which occurs due to asymmetries in the cantilever geometry and its mounting on the chip. Also the shape of the tip, which influences the contact area, is not known accurately enough, and may be not spherical as assumed in the equations above. It may not be even of rotational symmetry because it is a single crystal, and it may change its shape during experiments because of tip wear. The lateral stiffness of the tip is not known, so that till now, it is difficult to obtain the same lateral contact stiffness k^*_{lat} from different torsional modes of the cantilever.

Interesting yet little explored effects occur at high-excitation amplitudes [20]. The amplitudes push the tip into the attractive part of the force-distance curve. The flexural cantilever vibrations are then influenced by adhesion and the contact-resonances show highly non-linear behavior and hysteresis. Likewise, it has been recently that high-amplitude torsional vibrations cause slip in the tip-sample contact and thus contain friction forces [13].

In the piezo-mode, the sample surface vibrations, which generate the cantilever oscillations, are excited locally via the inverse piezoelectric effect. Thus, the local piezoelectric activity of the sample mainly contributes to the contrast in piezo-mode images. This part is superimposed by elastic and adhesive tip-sample interactions. As said above contact resonances of the cantilever can be exploited for image contrast enhancement in the piezo-mode. Ferroelectric domains in the sample polarized perpendicularly to the surface, when excited in the piezo-mode, cause out-of-plane surface vibrations which induce flexural cantilever vibrations [14, 15]. It has been shown that in-plane polarized ferroelectric domains, when excited in the piezo-mode, add a lateral vibration component [21] generating torsional cantilever resonances as well [17]. The local electric and strain fields at the sensor tip are extremely inhomogeneous accounting for a complicated quantitative evaluation. The main parameters playing a role in the imaging quantities are discussed in [14].

Results: The dynamic AFM methods have been applied to many different materials, e.g., crystalline materials [11], multi-domain ferroelectric ceramics and thin films [14, 15], polymeric materials [9, 18], nanocrystalline magnetic thin films [22], diamond-like carbon layers [23], and clay in rocks [24] have been examined. Friction and stick-slip phenomena have been studied by measuring the torsional resonances of the cantilever, for example in bare and lubricated silicon samples [25].

Fig. 1 shows the topography and an AFAM contact-resonance image of a nanocrystalline Ni sample with a grain size of 167 nm. The cantilever spring constant was 48 N/m, the first two free flexural resonance frequencies were 166 kHz and 1031 kHz, respectively. The contact-resonance image was taken with the first flexural mode. The image size is 1.5×1.5 μm^2. The flexural contact resonances yield the vertical contact stiffness (Fig. 2, image size 1.5×1.4 μm^2) and finally the local indentation moduli M. The results at the three points indicated in Fig. 2 are 234 (1), 184 (2), and 176 GPa (3), respectively. The data agree with indentation moduli calculated from literature values of Ni single crystal constants for different crystal orientations: $M_{(111)}$ = 223 GPa, $M_{(110)}$ = 218 GPa, $M_{(100)}$ = 202 GPa. A point by point quantitative comparison is not possible yet because the crystal orientations at the indicated positions are not known. Fig. 3 shows the topography and vertical (f = 332 kHz, 1st bending mode) and lateral (f = 3.1 MHz, 1st torsional mode) piezo-mode images (size: 6×6 μm^2) of a piezoelectric ceramic (Lead Zirconate Titanate, PIC 151). A Pt-Ir coated cantilever, spring constant k_c = 2.3 N/m, first two free bending resonances f_1 = 69.2 kHz and f_2 = 435.5 kHz, was used. In contrary to the topography image, in the piezo-mode images ferroelectric domains of different polarization are visible.

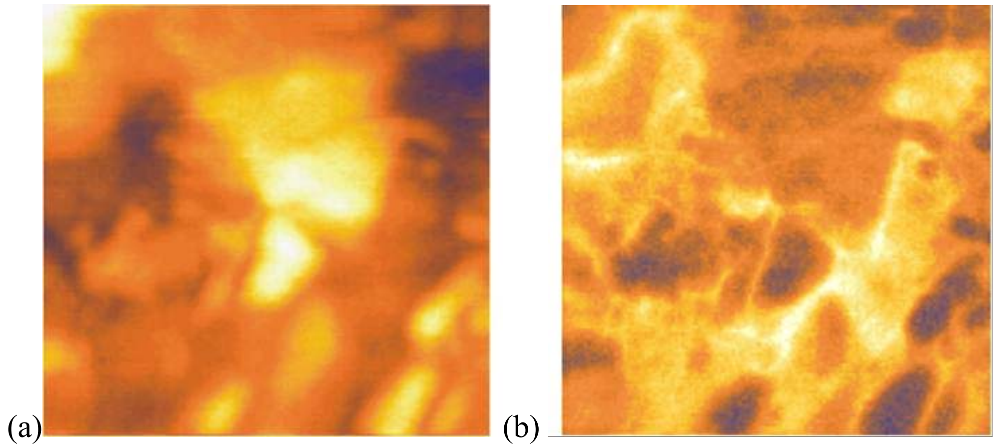


Figure 1: (a) Topography, height scale 10 nm, (b) contact-resonance AFAM image, frequency scale 730 – 750 kHz, of nanocrystalline Ni.

Conclusions: The quantitative evaluation of the contrast of dynamic AFM images in order to determine local material properties is still a challenge. The contact resonance spectroscopy allows one to deduce elastic constants such as the indentation and the shear modulus from flexural and torsional contact resonance frequencies provided that low enough excitation amplitudes are used permitting to linearise the interaction force. Absolute measurement accuracy is at present ≤ 30%, especially when stiff materials are investigated. The relative accuracy within an image is better than 5 %. A quantitative analysis of the nonlinearity of the interaction forces in AFAM to determine adhesion and friction parameters and of the piezo-mode to obtain local piezoelectric is the subject of ongoing research projects.

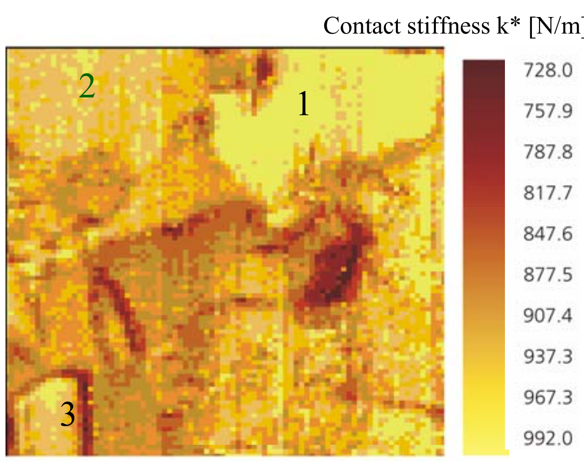
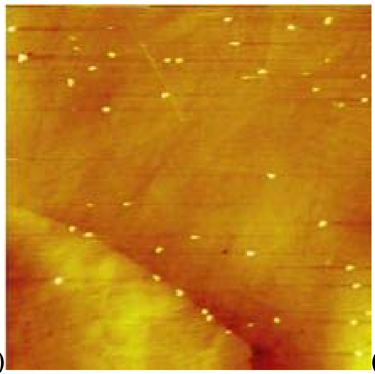
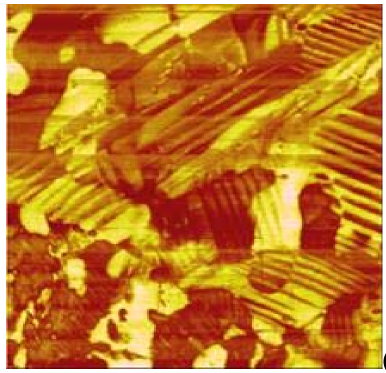


Figure 2: Contact-stiffness AFAM image of Ni

(a)  (b)  (c)

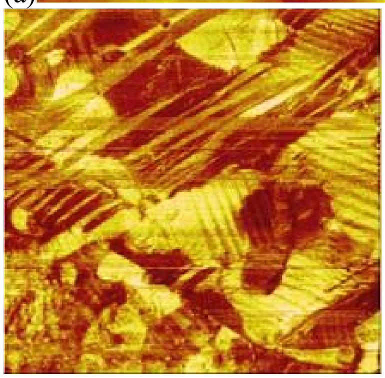


Figure 3: a) Topography, height scale 20 nm, b) vertical and c) lateral piezo-mode images of PIC 1

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