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A measurement system for nonlinear surface spectroscopy with an atomic force microscope during corrosion process monitoring

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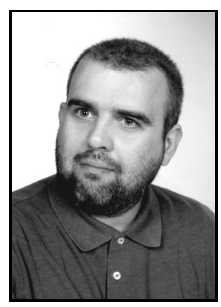

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Abstract

In addition to traditional imaging of the surface, atomic force microscopy (AFM) enables wide variety of additional measurements. One of them is higher harmonic imaging. In the tapping mode the nonlinear contact between a tip and specimen results in higher frequency vibrations. More information available from the higher harmonics analysis proves to be helpful for more detailed imaging. Such visualization is especially useful for heterogeneous surfaces which are studied to understand corrosion mechanisms. In this paper the measurement system for nonlinear surface spectroscopy by AFM for corrosion processes monitoring is presented.

Keywords: corrosion, atomic force microscopy, synchronous detection, nonlinearity.

System pomiarowy do nieliniowej spektroskopii powierzchni mikroskopem sił atomowych podczas monitorowania procesów korozji

Streszczenie

Oprócz tradycyjnego zastosowania, mikroskop sił atomowych (ang. *Atomic Force Microscope*, AFM) [1] (rys. 1) umożliwia wiele dodatkowych pomiarów, wśród których wyróżnić można obrazowanie powierzchni próbki wyższymi harmonicznymi [6-13]. W trybie półkontaktowym [2-4] w odpowiedzi mikrobelki zauważane są wyższe harmoniczne będące wynikiem oddziaływań nieliniowych [2-6]. Wykorzystanie wzmacniacza fazoczułego (ang.: lock-in amplifier) umożliwia obrazowanie topografii badanej próbki [12, 13] nawet do dwudziestej harmonicznej. Otrzymywane obrazy umożliwiają wyostrzenie elementów niewidocznych podczas tradycyjnego skanowania. Ma to związek z wyostrzoną czułością wyższych harmonicznych na struktury topograficzne. Takie obrazowanie jest szczególnie przydatne do badań próbek niejednorodnych [12], gdy łatwo wyróżnić przez obserwację poziom niektórych harmonicznych [6]. Oprócz wyraźnych zmian przy przejściach między różnymi substancjami, pomiary w cieczach wykazują się zwiększoną wrażliwością na lokalne różnice w elastyczności i interakcji geometrii [10]. Przedstawiono system do obrazowania powierzchni za pomocą wyższych harmonicznych w pomiarach ECAFM (ang. *Electrochemical Atomic Force Microscopy*, ECAFM, rys. 2). Prezentowane rozwiązanie (rys. 3, rys. 4) umożliwia jednoczesną rejestrację obrazów do szóstej harmonicznej podczas monitorowania procesów korozji (rys. 5, 6). Proponowany system pozwala na uzyskiwanie dodatkowych informacji o zjawiskach korozji zachodzących na skanowanych powierzchniach. Taka metoda stanowi uzupełnienie istniejących metod analizy powierzchni korozyjnych [14-16].

Słowa kluczowe: korozja, mikroskop sił atomowych, detekcja synchroniczna, nieliniowości.

1. Introduction

An atomic force microscope (AFM) [1] is one of the surface topography imaging methods in the nanoscale. The AFM uses a cantilever beam to place a small scanning tip in close proximity to the sample. The cantilever is a tip-sample force-sensing device [2] which creates a topography map of the specimen. Typically, the force is measured as deflection of the cantilever detected by a laser beam (Fig. 1). This measurement method enhances our ability to characterize materials, map variations in chemical composition, and investigate the properties of nanostructures.

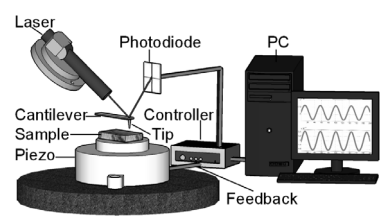

Fig. 1. Schematic illustration of the AFM
Rys. 1. Schemat budowy AFM

In the standard surface characterization the dynamic AFM (DAFM) is mostly used. Dynamic modes are observed in tapping-mode (TMAFM) where the tip briefly interacts with a sample once per the oscillation cycle. There are two fundamental measurement methods based on TMAFM. The first one is the determination of surface properties by measuring a phase lag between excitation and response signals. However, interpretation of this phase imaging is still discussed. The other one is the detection of higher

harmonics of excitation frequency, present in the response signal [3-5]. Intensities of the higher harmonics correspond to nonlinearity of the tip-sample forces [6].

2. Theoretical background

The vibrating cantilever can be considered as a linear system because of its small amplitude of oscillations when compared with its dimensions [7]. The equation of motion of a cantilever tip can be approximated by a one-dimensional forced harmonic oscillator with damping, yielding the nonlinear, second order differential equation [3]:

$$m\ddot{x} + \frac{m\varpi_0}{Q}\dot{x} + kx = F_0\cos(\varpi t) + F_{ts}(d_{ts}) \tag{1}$$

where:

m - mass of the free cantilever,
Q - quality factor of the free cantilever,
k - force constant of the free cantilever,
ω_0 - angular resonance frequency of the free cantilever,
ω - angular frequency of the driving force at time t,
F_0 - amplitude of the driving force at time t,
$F_{ts}(d_{ts})$ - tip surface interaction force,
d_{ts} - tip-sample distance.

F_{ts} is a sum of the attractive van der Waals force and the repulsive force due to elastic interactions between the tip and the surface, represented by Lennard-Jones force function. In long-range intermolecular distance a_0, close to the surface ($a_0 \le d_{ts}$), the electrostatic force can be neglected. Thus, F_{ts} is represented only by the van der Waals force. When the tip has contact with the surface ($a_0 \ge d_{ts}$), the elastic interaction of the tip should be included. So that systems without energy dissipation can be modeled using Derjaguin-Müller-Toporov (DMT) [7-10]:

$$F_{ts}(d_{ts}) = \begin{cases} -\dfrac{HR}{6d^2_{ts}} & for \quad d_{ts} \ge a_0 \\ -\dfrac{HR}{6d^2_{ts}} + \dfrac{4}{3}E\sqrt{R}(a_0 - d_{ts})^{3/2} & for \quad d_{ts} \le a_0 \end{cases} \tag{2}$$

where:

H - Hamaker constant,
R - the tip radius,
E - combined Young modulus of the tip (effective contact stiffness) [3]:

$$E = \left(\frac{1-v^2_t}{E_t} + \frac{1-v^2_s}{E_s}\right)^{-1} \tag{3}$$

where:

E_t - elastic moduli of the tip,
E_s - elastic moduli of the sample,
v_t - Poisson ratio of the tip,
v_s- Poisson ratio of the sample.

The Eq. (1) have to be expanded by the additional factor representing a force acting on the cantilever when oscillating at a separation d_{ts} to the surface in liquid [10]:

$$m\ddot{x} + \frac{m\varpi_0}{Q}\dot{x} + kx = F_0\cos(\varpi t) + F_{ts}(d_{ts}) + F_{hyd}(d_{ts}) \tag{4}$$

The nonlinearity of Eq. (2) causes generation of higher harmonics in the cantilever oscillations. The shape of F_{ts} force function is determined by local physical properties of the specimen. This fact should be helpful in recognition of transition between different parts of the investigated surfaces. Identification of such transitions is especially important during corrosion process monitoring. Those measurements are performed by electrochemical AFM (ECAFM). That method required a dedicated adapter enabling insertion of the sample in the electrolyte under the controlled potential (Fig. 2).

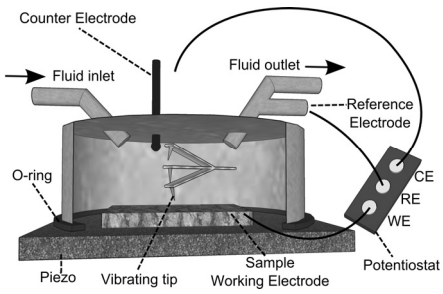

Fig. 2. Schematic illustration of ECAFM
Rys. 2. Schemat budowy ECAFM

3. Measurement system

In order to provide higher harmonics measurements, the corresponding signals should be observed. The excitation signal from a generator (GEN) and the cantilever response from a photodiode (DFL) (Fig. 3) are recorded by the data acquisition board. Moreover, it is necessary to record the synchronization signal, which is significant to recognize when every single pixel is scanned. After recording of these tree signals for the scanned structure, the data are processed by a dedicated software. During processing the fragments of excitation and response signals are separated for every single pixel. In the next step a software lock-in amplifier to detect higher harmonics was used (Fig. 4). The final image is created by combining the lock-in amplifier calculations.

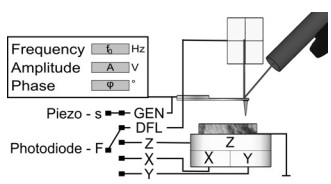

Fig. 3. Parameters of the excitation GEN and measuring response signal DFL
Rys. 3. Parametry sygnału pobudzenia GEN i mierzona odpowiedź dźwigni DFL

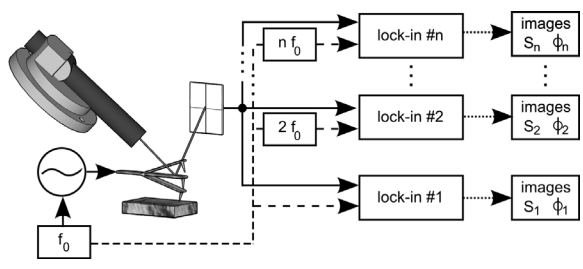

Fig. 4. Higher harmonics detecting by a lock-in amplifier
Rys. 4. Wykrywanie wyższych harmonicznych za pomocą wzmacniacza fazoczułego

The system was described in detail in the previous works [11, 13]. Such measurements require specialized microscopic probes [12] or are limited to an image of the selected harmonic. The presented solution is more general and determines images for a few different harmonics. The previous works [11, 13] proved that the described measurement system worked properly. Fig. 5 shows the sample of glass fiber embedded in resin. Fig. 6 presents the same specimen visualized by higher harmonics images with the area invisible in traditional pictures and marked by the striped line.

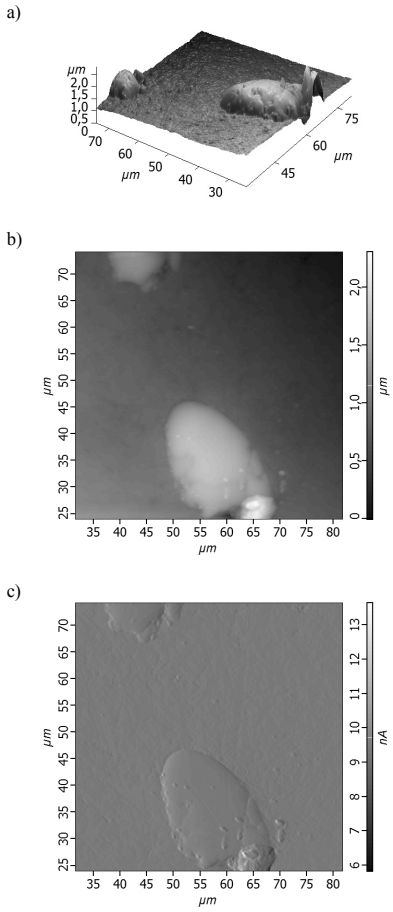

Fig. 5. The sample of glass fiber embedded in resin: a) three dimensional picture, b) topography, c) control error
Rys. 5. Obraz próbki włókna szklanego w żywicy: a) obraz trójwymiarowy, b) topografia, c) sygnał sprzężenia zwrotnego

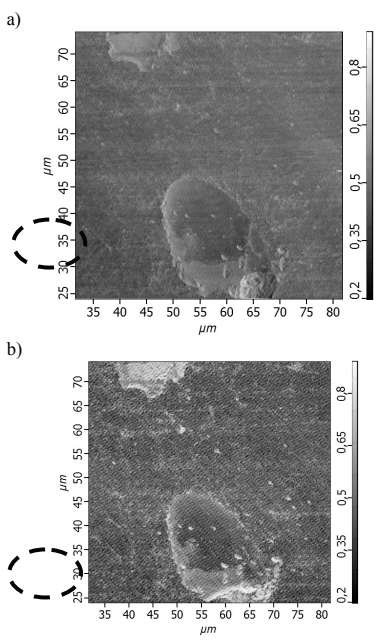

Fig. 6. Higher harmonics images: a) amplitude of the second harmonic b) amplitude of the sixth harmonic
Rys. 6. Obrazy wykonane za pomocą wyższych harmonicznych: a) drugiej, b) szóstej

The proposed measurement technique gives some additional information about physical properties of the scanned surface but there is no clear relation between higher harmonics components and physical properties of the studied structure. We hope that this method can be successfully applied to characterize a corroding sample but further and more thorough investigation is necessary to establish relations between higher harmonics and physical properties of the investigated sample. Fortunately, we can expect identification by images of higher harmonics of the locally charged area which are caused by varied corrosion intensity and its stage. The charged area will influence the force between the specimen and the tip and therefore will influence the intensity of nonlinear effects. As a result such method would characterize the corroding sample in a more efficient way, which is important in any scientific field related to anticorrosion protection [14-16].

4. Conclusions

The presented results lead to increased functionality of the atomic force microscope by using the developed measurement system. The system can be applied to various atomic force microscope systems at relatively modest costs. Such measurements should provide additional information about corrosion processes taking place on the scanned surface and assure better characterization of their physical properties.

5. References

[1] Binning G., Quate C. F., Gerber C.: Atomic force microscope. Physical Review Letters 56, 1986.
[2] Garcia R., San Paulo A.: Attractive and repulsive tip-sample interaction regimes in tapping-mode atomic force microscopy. Physical Review B 60, 1999.
[3] Garcia R., Pèrez R.: Dynamic atomic force microscopy methods. Surface Science Reports 47, 2002.
[4] Garcia R., San Paulo A.: Dynamics of a vibrating tip near or in intermittent contact with a surface. Physical Review B 61, 2000.
[5] Lee S. I., Howell S. W., Raman A., Reifenberger R.: Nonlinear dynamics of microcantilevers in tapping mode atomic force microscopy: A comparison between theory and experiment. Physical Review B 66, 2002.
[6] Sahin O., Quate C. F., Solgaard O.: Resonant harmonic response in tapping-mode atomic force microscopy. Physical Review B 69, 2004.
[7] Stark R. W., Heckl W. M.: Higher harmonics imaging in tapping-mode atomic-force microscopy. Review of Scientific Instruments 74, 2003.
[8] Stark R. W.: Spectroscopy of higher harmonics in dynamic atomic force microscopy. Nanotechnology 15, 2004.
[9] Hillenbrand R., Stark M., Guckenberger R.: Higher-harmonics generation in tapping-mode atomic-force microscopy: Insights into the tip–sample interaction. Applied Physics Letters 76, 2000.
[10] Preiner J., Tang J., Pastushenko V., Hinterdorfer P.: Higher Harmonic Atomic Force Microscopy: Imaging of Biological Membranes in Liquid. Physical Review Letters 99, 2007.
[11] Babicz S.: The study of harmonic imaging by AFM. Pomiary Automatyka Kontrola 12, 2011.
[12] Sikora A., Bednarz Ł.: The implementation and the performance analysis of the multi-channel software-based lock-in amplifier for the stiffness mapping with atomic force microscope (AFM). Bulletin of the Polish Academy of Sciences: Technical Sciences 60, 2012.
[13] Babicz S., Zieliński A., Smulko J.: Enhancing capabilities of Atomic Force Microscopy by tip motion harmonics analysis. Bulletin of the Polish Academy of Sciences: Technical Sciences 61, 2013 (during the issue).
[14] Hoja J., Lentka G.: Analyzer for spectroscopy of low impedance. Metrology and Measurement Systems XVI (1), 2009.
[15] Niedostatkiewicz M., Zielonko R.: Investigation on accelerated impedance spectrum measurement method with mulisine signal stimulation objects. Metrology and Measurement Systems XVI (4), 2009.
[16] Antoniuk P., Strąkowski M., Pluciński J., Kosmowski B.: Non-Destructive Inspection of Anti-corrosion protective coatings using optical coherent tomography. Metrology and Measurement Systems XIX (2), 2012.

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