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UTILIZATION OF AFM MAPPING OF SURFACE'S MECHANICAL PROPERTIES IN DIAGNOSTICS OF THE MATERIALS FOR ELECTROTECHNICS

ABSTRACT *Atomic force microscopy (AFM) is one of the most powerful diagnostic methods used in micro- and nanoscale imaging of the topography and various physical properties of the surface. As this method involves the scanning tip/sample interaction, it is possible to observe the response of the surface on periodically changing load causing by the scanning tip. By utilizing so called time-resolved tapping mode, we could perform the mapping of the surface's mechanical properties: stiffness, adhesion, energy dissipation and others. In this paper we present the idea of the NanoSwing imaging technique developed at Electrotechnical Institute, Division of Electrotechnology and Materials Science in Wrocław as well as the examples of the measurement results.*

Keywords: *atomic force microscopy, time-resolved tapping mode, mechanical properties mapping, nanomaterials, material science.*

1. INTRODUCTION

Continuous progress in material science is aimed at implementation of nanomaterials, as their properties can significantly differ from traditional materials.

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Due to presence of certain particles of the size below of 100 nm in at least one dimension, new generation materials can exhibit better environmental conditions resistance (solar irradiance resistance, cold/heat resistance), as well as the mechanical (stiffness, wear resistance, mechanical shock resistance) and electrical (resistivity, permittivity, dissipation factor) properties. It is crucial however, that during the new material development process, appropriate feedback should be provided in order to obtain desired information about the structure of the material and its certain properties. As the subnanometer resolution diagnostic methods are necessary in order to deliver relevant data, during last few decades one could observe a significant progress in the development of various measurement techniques allowing imaging of the properties of various materials.

Atomic force microscopy is one of the high resolution imaging techniques allowing to investigate various properties of the surface with submicrometer – subnanometer resolution [1]. This method bases on the observation of the interaction between the sample and the very sharp scanning tip, which during scanning process acts as the near field forces sensor. Therefore it can experience a wide spectra of short and long range interactions such as: Van der Waals, adhesion, electrostatic, magnetic forces. By implementing a particular detection technique and utilization of the scanning tip model, one can selectively detect specific force in order to correlate it with particular properties of the sample [2].
In order to observe the tip-sample interaction, the cantilever integrated with the tip is used, as its elastic deformation is related to acting force (Fig. 1). By using the laser-cantilever-photodiode optical detection system, the force can be measured, transformed into the electrical signal and utilized in the imaging process. The piezoactuator based, precise X-Y-Z positioning system provides the movement of the tip in respect to the sample. The controller and the computer acquire the electrical signals, collect, process and display the measurement data.

As the tip is used as the near field forces sensor, it is utilized in the surface profiling, therefore the basic information that AFM system delivers is the topography map of scanned area. It is worth of mentioning, that the morphology data can deliver precious information about the atomic or macromolecular ordering of the material. Nevertheless such data is sometimes insufficient, therefore additional parameters should be measured in order to reveal certain properties of the material. As the mechanical properties as the stiffness or the adhesion can reveal the complexity of the material's structure and allow to interpret the correlation between the technological parameters and the macroscopic properties, there is a particular interest in development of a high resolution and fast mapping modes.

Since the first demonstration of the atomic force microscopy [3], the number of scanning probe-based techniques have been introduced [2]. In terms

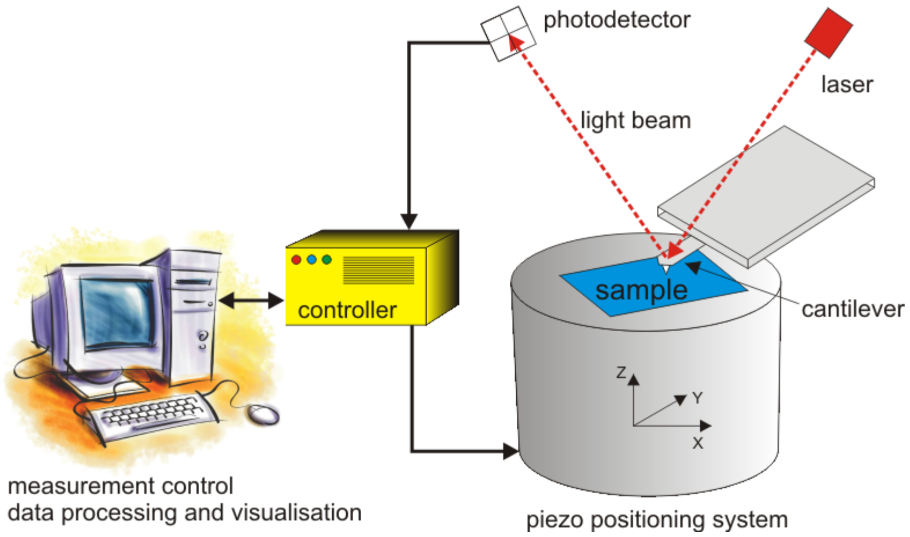

Fig. 1. The simplified diagram illustrating the construction of atomic force microscope showing most important components of the measurement system

of investigating the mechanical properties of the surface, one can point out such modes as: Lateral Force Microscopy [4], Force Modulation Microscopy [5], Force Volume Microscopy [6], Jumping Mode Scanning Force Microscopy [7], Digital Pulse Force Mode [8]. It should be underlined, that due to certain disadvantages such as: large applied force causing modification of the surface, low scanning speed or low mapping resolution, new techniques are desired. The *NanoSwing* mode developed at Electrotechnical Institute [9] overcomes abovementioned disadvantages, as it bases on time-resolved tapping mode method, where the detection and complex processing of the torsional oscillations of the cantilever is performed in order to determine local mechanical properties of the surface.

2. ANALYSIS OF TORSIONAL BENDING OF THE CANTILEVER IN MAPPING OF THE MECHANICAL PROPERTIES OF THE SURFACE

In order to perform mapping of the mechanical properties of the surface, the tip-sample interaction must be observed and analyzed. The *NanoSwing* mode is the imaging method derived from tapping mode technique [10-11], as the tip oscillates perpendicularly to the surface and touches it for certain amount of time. It should be underlined, that as the typical tapping mode is utilized, one is able to acquire the phase shift between the excitation signal and the response of the cantilever. This Phase Imaging feature can reveal differences in energy dissipation on the surface [12]. It is however very difficult to interpret the results, due to complexity of detected interactions as well as signal processing method. Therefore more advanced and reliable method is required.

As the tip moves back and forth within attractive and repulsive forces ranges (Fig. 2), it can detect various kinds of interactions, therefore certain mechanical properties of the surface can be determined. In order to provide desired quality of cantilever's response, specific construction of this sensor was developed and presented by Sahin et al. [13]. As the scanning tip is moved away from the symmetry axis (Fig. 2), the torque is sufficient to make the cantilever bend, therefore the torsional bend can be measured and analyzed.

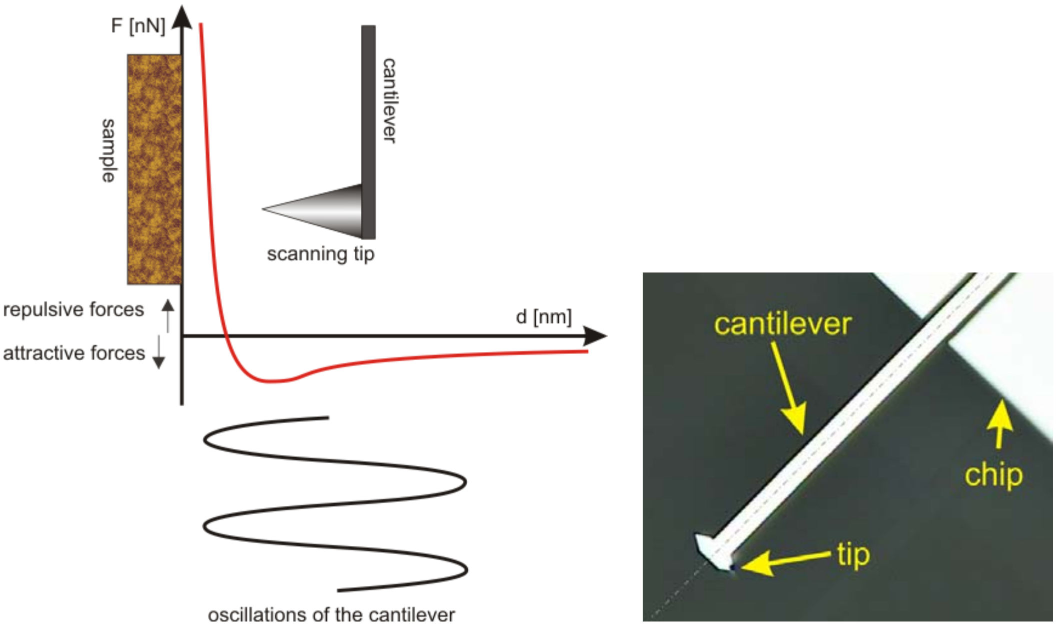

Fig. 2. The tip-sample forces graph with correlated path of the cantilever's oscillation
Some of the proportions have been disturbed in order to provide good readability of the curves (left). The optical microscope view of the T-shaped cantilever (right). The arrows point at the locations of the specific parts, including the hammer-shaped end of the cantilever with the asymmetrically placed tip.

As in typical AFM setups, the quadrant photodiodes are utilized, both: flexural and torsional bending of the cantilever can be acquired (fig. 3). In order to detect the flexural bending, the signals should be processed as follows: D1+D3-D2+D4. In case of torsional oscillations, the operation D1+D2-D3+D4 should be performed.

One must be aware, that in order to observe all significant events that occur during signal oscillation of the cantilever, high sampling data acquisition must be performed [9, 14-16]. Additionally, due to complexity of acquired torsional signal, advanced signal processing involving real time FFT filtering and DMT (Derjaguin-Muller-Toporov) model [17] curve fitting must be carried out. Finally, as the force-distance curve containing the approach (A1-A3) and retract (R1-R3) features related to certain tip-sample interactions is reconstructed, one can extract such properties as: stiffness, adhesion and energy dissipation (Fig. 3).

As the scanning process is performed, the values of certain parameters are stored in the memory of the computer as the X-Y matrix data sets, which are correlated to the topography map. Eventually, one obtains the set of maps representing the mechanical properties of the surface, which can be used in interpretation process, delivering desired information about the sample. It should be mentioned, that in general, the brighter color on created map is related to the higher value (height, force, stiffness, voltage and so one). Additionally the color bars placed next to the pictures can make the observation easier, however this feature can be omitted accidentally or on purpose by some authors (when the qualitative information is not available).

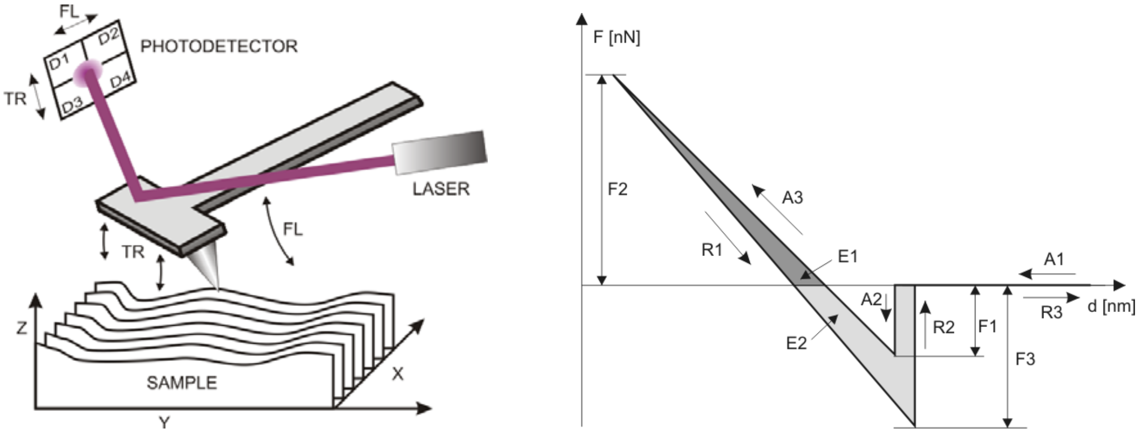

Fig. 3. The idea of scanning the surface with the T-shaped cantilever allowing to observe its flexural and torsional oscillations (left) as well as the optical detection system of the flexural (LF) and torsional (TR) oscillations. Typical force spectroscopy curve and the related mechanical properties of the surface (right). The parameters are: F1 – snap-in force, F2 – peak force, F3 – adhesion. R1 (slope) – stiffness, E1 – energy dissipation for deformation, E2 – energy dissipation for tip-sample separation

Usability of the time-resolved tapping mode imaging technique implemented in commercially available setup was presented by various groups in the material science [18, 19] where the non-homogenous materials were investigated as well as in the biological science in detection of certain molecules with single atto-molar sensitivity [20]. Also the investigation of the bacterial nanowires [21] was presented in terms of their utilization in technical applications.

3. EXAMPLES OF THE MEASUREMENTS

The examples of the measurement results are presented in following figures. One of the materials that is recently carefully investigated due to its promising properties, is the polyazomethine, which can be utilized as one of the main components of various sensors. As this material exhibits the properties of liquid crystal, one can expect the presence of molecular ordering. The morphology didn't reveal any particular structures (Fig. 4), therefore the maps of mechanical

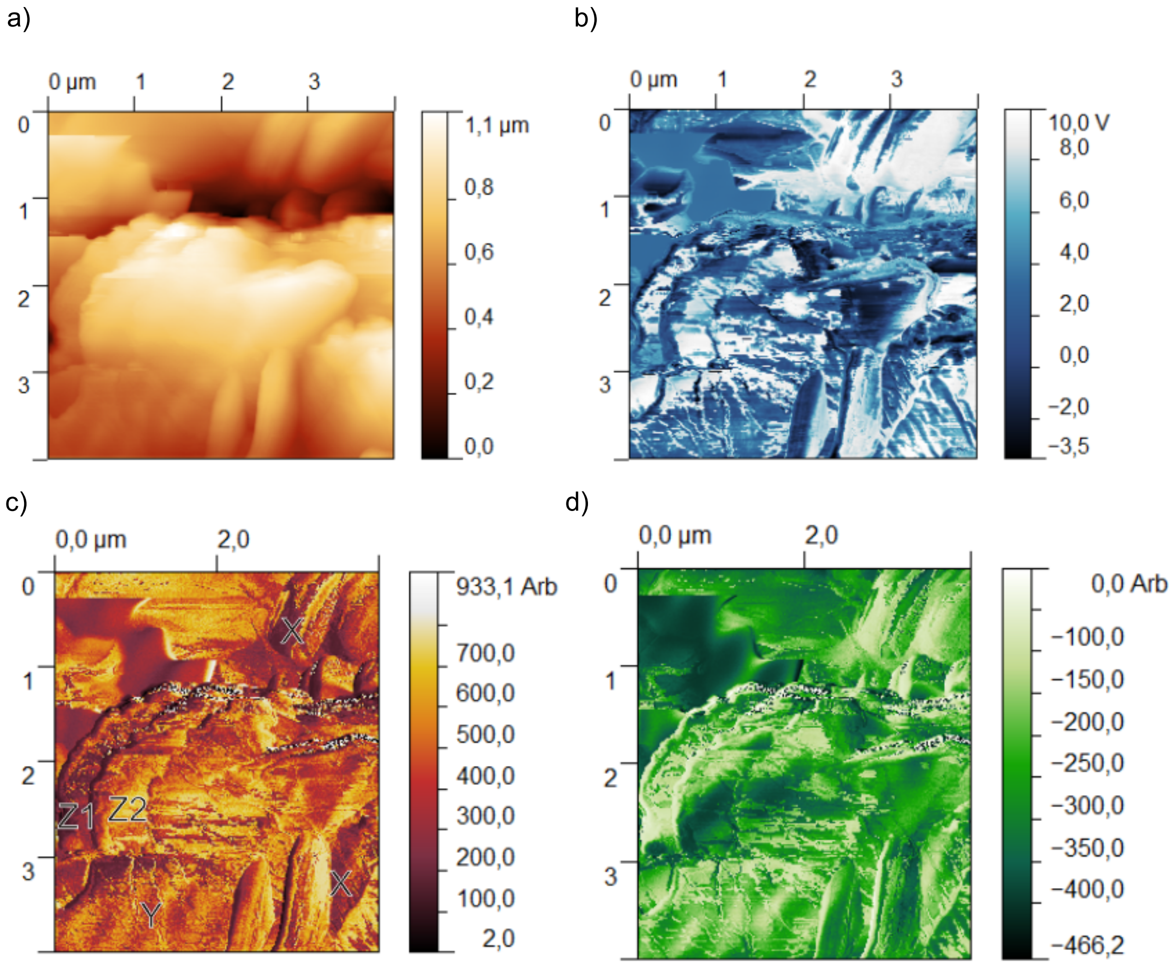

Fig. 4. Results obtained during the measurement of the polyazomethines sample
Topography (a), phase image (b), stiffness (c) and adhesion (d)

properties become the source of valuable data. The phase image, related to the tip-sample energy dissipation, allowed to observe some kind of structures, but details however are not visible good enough. Additionally, it is difficult to interpret such information in terms of determining the origin of varying the tip-sample interaction. The stiffness map revealed much more detailed structures, therefore it was possible to notice the lamella structure of long objects located in right-top and right-bottom corners marked with X's (Fig. 4c). In the left bottom corner one can see the less regular, grainy structure (Y). Additionally, the terraces reveal different stiffness values. The lower terrace is softer (Z1), than the higher ones (Z2). This phenomena can be connected to the fact, that certain thickness of the material is necessary to obtain specific stiffness. The adhesion map shows slightly different features, however it is typical that those two qualities are related to each other. The grainy structures are not visible here, as adhesion forces can interact with the tip on larger distance, therefore it covers larger area due to worse spatial resolution. Observed brighter-darker planes can be related to the macromolecular ordering (single step-layers), which reveal various functional groups, therefore the pull-off force can vary. Such phenomena can be confirmed by the molecular modeling.

Another example is the graphene layer deposited on silicon dioxide substrate with exfoliation method [22]. The monolayer could be identified with an optical microscope, and in the next step with the AFM height measurement. As during the exfoliation process, complex structures can be obtained, we've measured the mono- and multilayer flake in order to observe the influence of the thickness on the mechanical properties of this exciting and promising material. The topography (Fig. 5a) reveals presence of the monolayer as well as the multilayer areas. The profile (Fig. 5c) confirmed the preliminary conclusion concerning the number of layers. Additionally, the phase image shows clearly area of the presence of graphene. Observation of the stiffness map (Fig. 5d) allowed to conclude that the graphene monolayer is stiffer than the silicon dioxide (according to the literature, graphene: 500-950 GPa, SiO2: 40-95 GPa), and the number of layers does not have the influence on the stiffness. Our observation confirmed extraordinary properties of the single layer of graphene. The peak force (Fig. 5e) however didn't reveal any non-homogeneities. It could be predicted, as both materials are stiff enough to exhibit similar mechanical response on applied load. The adhesion (Fig. 5f) allowed to observe smaller forces over graphene surface, which can be connected to the specific chemical bonding phenomena as well as the wettability of observed surfaces. Further observations are necessary to identify its origin. It should be underlined, that due to limited range of the stiffness detection (up to 100 GPa), related to the spring constant of the cantilever, it was not possible to acquire the quantitative measurement data.

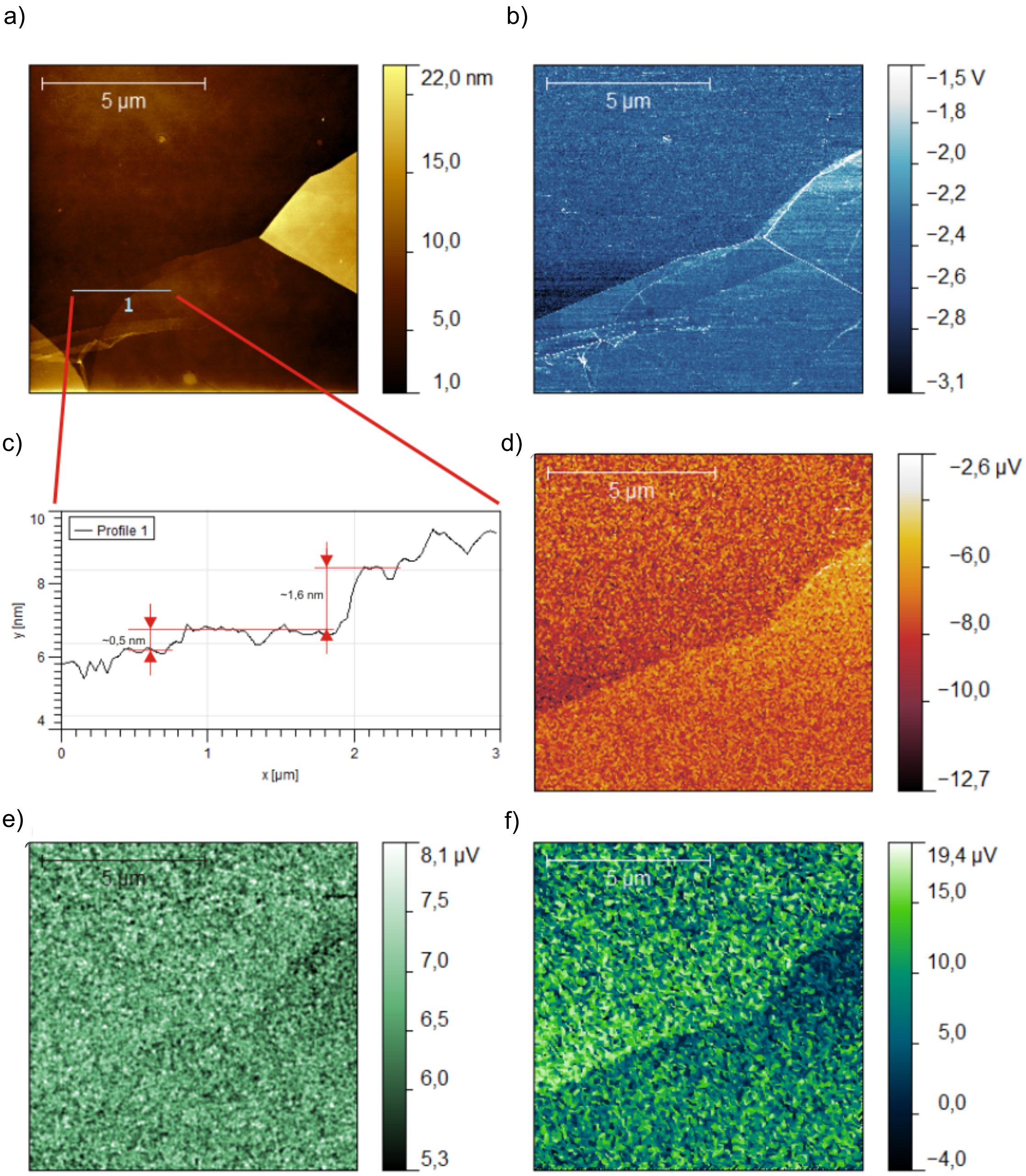

Fig. 5. Results obtained during the measurement of the graphene on silicon dioxide substrate Topography (a), phase image (b), the profile of the topography image along indicated line (c), stiffness (d), peak force (e) and adhesion (f)

4. SUMMARY AND OUTLOOK

In this paper we've presented the utilization examples of advanced AFM mapping method of the surface's mechanical properties. The measurement examples, allowed to prove that the scanning tip can be utilized as the sensor of the mechanical properties of the surface at nanoscale. The *NanoSwing* mode, by advanced signal processing can deliver far more valuable data than phase imaging technique. Further development of the above described method is planned in order to increase its detection resolution as well as to add further maps revealing the tip-sample interaction in terms of using this information during the validation of the measurement.

The spectra of the materials utilized in electrotechnics is very wide, therefore one can expect that the high resolution mapping method will be widely utilized in nanomaterials research.

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WYKORZYSTANIE MAPOWANIA WŁAŚCIWOŚCI MECHANICZNYCH POWIERZCHNI TECHNIKAMI AFM W DIAGNOSTYCE MATERIAŁÓW STOSOWANYCH W ELEKTROTECHNICE.

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STRESZCZENIE *Mikroskopia sił atomowych (AFM) jest jedną z najbardziej zaawansowanych technik diagnostycznych w mikro- i nanoskali, stosowaną w procesie obrazowania topografii oraz różnych właściwości fizycznych powierzchni. Wykorzystanie oddziaływania ostrze* *skanujące-próbka umożliwia obserwację odpowiedzi materiału na okresowe zmiany nacisku wywoływane przez ostrze, dzięki czemu możliwa jest ocena właściwości mechanicznych próbki. Zastosowanie trybu dynamicznego z analizą oscylacji skrętnych belki skanującej w domenie czasu, umożliwiło wykonywanie mapowania takich parametrów jak: sztywność, adhezja, rozpraszanie energii i inne. W niniejszej pracy zaprezentowano koncepcję działania trybu NanoSwing opracowanego we wrocławskim oddziale Instytutu Elektrotechniki. Przedstawiono także przykładowe wyniki pomiarów wykonanych z wykorzystaniem tego trybu.*