Optica Applicata, Vol. XLIII, No. 1, 2013
DOI: 10.5277/oa130120

Development and utilization of the nanomarkers for precise AFM tip positioning in the investigation of the surface morphology change

ANDRZEJ SIKORA

Electrotechnical Institute, Division of Electrotechnology and Materials Science,
M. Skłodowskiej-Curie 55/61, 50-369 Wrocław, Poland; e-mail: sikora@iel.wroc.pl

The investigation of the surface properties changes at micrometer and nanometer scale, due to the presence of various factors such as: temperature, solar radiation or magnetic field, requires suitable diagnostic methods. Atomic force microscopy (AFM) is one of the most popular measurement techniques providing necessary resolution. As complex experiments may require multiple moving of the sample between instruments and AFM, one can find quantitative comparison of the results unreliable when the measurements are performed without precise positioning of investigated surface and different areas are analyzed.

In this work, the utilization of the nanoscratching method in terms of development of the nanomarkers set is presented, as the solution for precise positioning of the sample in order to perform the multi-step imaging of small surface area (1 μm×1 μm). Various materials were used to verify the versatility of the developed method. Also, the observation of the influence of the UV radiation on the polycarbonate sample was demonstrated as the example proving the application potential of the approach.

Keywords: atomic force microscopy, material science, environmental tests, nanolithography, nanomarker.

1. Introduction

Continuous effort in the field of the material science focused at the development of new materials, requires among others, reliable verification of the influence of various factors on a fabricated object. The most common test considering the impact of environmental conditions bases on the simulated solar radiation [1, 2], as well as the high/low temperature and high/low humidity conditions [3, 4] exposure. As the nanomaterials become a significant and promising category of products, it is necessary to provide the information about the submicron degradation of the surface due to the exposure on certain factor. Therefore one requires a high resolution measurement tool, allowing to acquire desired data. One of the most popular instruments at nanoscale diagnostics is atomic force microscopy (AFM), which provides a wide range of measurement techniques, allowing to image mechanical, thermal, electrical, magnetic and optical proper-

ties of the surface. A number of successful observations of the morphology change due to the light/temperature or electrical field presence have been done with AFM [5–8].

As the environmental tests require to place the sample in a specially designed chamber, the verification measurement can be difficult to perform, as one needs to put a significant effort in repositioning of the sample in order to scan the same area of a few microns size and to obtain reliable information with the highest confidence. One can assume that the data acquired in various areas of the sample are representative and reliable, in such a case, the sample should be homogenous and no additional area-related issue should have an impact on the measurement. However, in order to perform the experiment without any risk of misinterpretation caused by unreliable data acquired during imaging of randomly selected areas, the subsequent measurements should be performed precisely in the same area.

As the solution, the set of markers can be placed on the surface of the sample in order to make the repositioning process fast, easy and reliable. It should be emphasized that the problem of precise sample positioning in AFM metrology was successfully solved by RITTER *et al*. [9], however in this case, advanced fabrication methods are utilized. Therefore another approach must be applied. As no appropriate method for the above mentioned problem was published yet, is was necessary to develop and verify adequate solution.

Concerning a wide spectra of the micro- and nanostructures fabrication techniques, one must take into account their unwanted impact on the surface, additional equipment access requirements as well as the time and the cost of the process. The scanning probe litography (SPL) methods, in particular, nanoindentation and nanoscratching techniques, are the most attractive ones, due to the local tip–sample interaction without any chemical solution being deposited on the surface and high precision of the process. The major advantage of this approach is that the same instrument can be utilized in both: markers fabrication and surface imaging. Although nanoscratching is mainly used for the development of functional nanostructures [10, 11] or tests of mechanical properties of the material [12, 13], it may be useful in machining at nanoscale [14–17] as well as fabrication of the set of nanomarkers.

In order to confirm the usability and versatility of proposed approach, the tests on various surfaces have been performed. The development of nanomarkers was successfully realized on such materials as: silicon/silicon dioxide, stainless steel, NiFe thin layer, polycarbonate, sheet moulding compound and epoxy resin. Additionally, in order to show practical applications of described solution, the polycarbonate surface roughness change caused by UV radiation was measured with high confidence, as the scanning field and quantitative analysis area were precisely defined due to the presence of developed structures.

2. Experiment

Experimental procedure contained two parts: the nanomarkers development on various materials and the simulation of the real test procedure. As the wear of the scanning tip

is a common problem when it is used for the mechanical modification of the sample, the diamond-coated tip probe was used as it is the most adequate for such a task due to its wear-resistance [16, 17]. DDESP model from Bruker was used with the following specific parameters: k = 42 N/m, f_{res} = 320 kHz, r_{tip} = 35 nm; tip coating: conductive diamond; material: 0.01–0.02 cm antimony (n) doped silicon; back coating: aluminum. The Innova AFM system with NanoPlot application from Bruker was used. The process was performed in ambient conditions.

The procedure was performed as follows: the surface was imaged using an intermittent contact mode in order to acquire the topography map, then the surface was modified according to a defined pattern, and finally the surface was imaged again in order to check whether the process was successful. The NanoPlot software allows to define the setpoint (oscillation amplitude of the tip) or the height offset referred to previously acquired topography as the nanoscratching parameter. Higher efficiency (structures depth and their repeatability) of the process was obtained in a height offset mode, which was applied in a range 5–45 nm. The speed of the tip was 0.3 µm/s.

Hard materials such as silicon/native silicon dioxide, electropolished stainless steel (AISI 304), and 180 nm thick NiFe layer deposited on glass substrate were tested successfully. No significant wear of the tip was noticed after the development of several sets of nanomarkers. The depth of the structures was in a range of 0.3–7 nm as the materials and parameters varied. Figure 1 shows the examples of the results of the nanoscratching procedure performed on silicon/silicon dioxide and stainless steel.

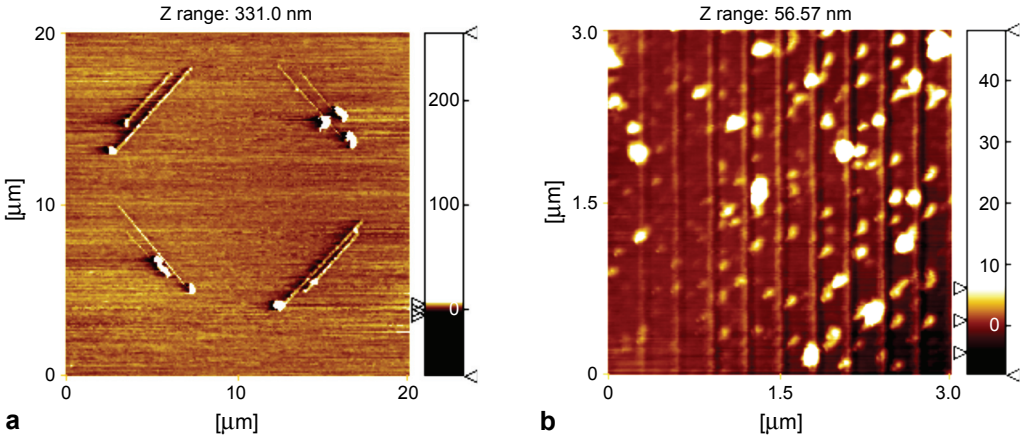

Fig. 1. Tests of nanoscratching procedure on silicon/silicon dioxide (**a**) and stainless steel surface (**b**).

Also relatively soft materials were tested: epoxy resin, sheet moulding compound and polycarbonate. The depth of the structures varied in a range of 5–65 nm. Due to higher roughness of such materials, deep markers are easy to find.

It must be underlined that as the scratches were fabricated, the material was pushed up or the flakes of the material were pulled out from the scratch. Therefore additional features appeared, which in this particular application were useful, as clearly

indicated the area of interest and allowed to find it relatively easily. The flakes however are highly undesired, as can attach to the tip and disturb the imaging process.

Figure 2 shows the examples of the results of the nanoscratching procedure performed on epoxy resin and polycarbonate. On the polycarbonate surface, the set of nanomarkers according to Fig. 3 was developed.

Figure 3 shows the simplified diagram of the nanomarkers set allowing fast and reliable positioning of the scanning tip within the area of a few micrometers. Such solution was tested in the second part of the experiment. The outer markers (A1–A4) can be placed in the corners of the maximum scan field of the microscope in order to cover as large area as possible and make the search process easier. It should be noted that the developed markers of a few microns in size can be visible with an optical microscope, therefore the positioning operation can be performed even faster.

The inner markers (C1–C4) show directly the scanned area (SA), providing a direct reference for the quantitative measurement of the roughness or other factors. The mid-

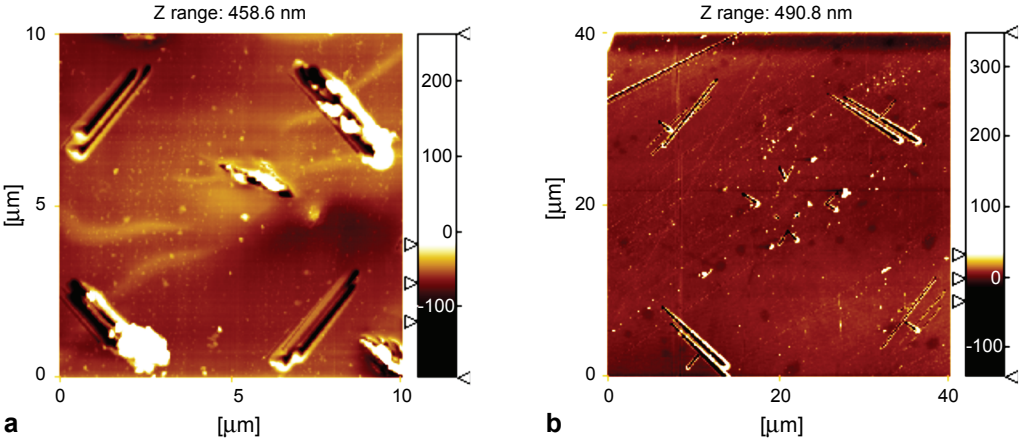

Fig. 2. Tests of nanoscratching procedure on epoxy resin (**a**) and polycarbonate surface (**b**).

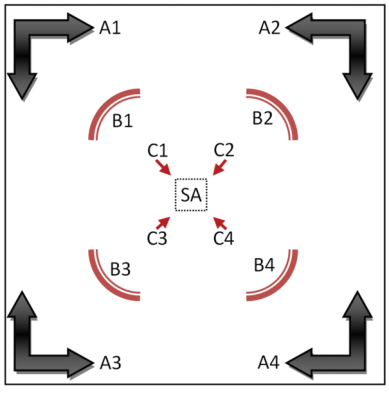

Fig. 3. The simplified diagram showing the set of nanomarkers allowing fast and reliable positioning of the scanning tip within the area of size 3 µm×3 µm.

dle markers (B1–B4) can be placed if necessary, in order to improve the positioning process and to increase the reliability of the procedure in case of damage of the inner markers.

It is essential that each marker should be easily identified in order to provide the information about the position of the scanned area. Therefore different shapes of the scratched features should be designed.

As the polycarbonate is a very popular material and it is utilized for production of the electronic components, construction materials, data storage carriers, automotive, aircraft and security components as well as medical equipment, it was used for the test of proposed diagnostic procedure.

The test of practical utilization of the nanomarkers was performed as follows: after performing the nanoscratch procedure, the optical image of the surface was taken in order to use it as the reference in the positioning process. Then, the sample was removed from the AFM and placed in the chamber with the set of LEDs emitting the radiation of the wavelength 405 nm. Calculated illuminance of the setup was 0.5 lux. After being exposed for 1700 hours, the sample was placed in AFM and positioned in order to scan the area indicated with the nanomarkers. As the surface was flat and homogenous and did not contain any intentionally placed structures, a few large debris were used for preliminary positioning procedure with an optical microscope. Then, the outer structures could be noticed in optical view of the scanning field. Further scans allowed to find the area of interest within a few minutes.

3. Results

Obtained results confirmed the efficiency of proposed measurement strategy. Once the outer nanomarkers were imaged using AFM, it was easy to determine the location of the area of interest, as each marker is unique and allows to define the position of the rest of the set.

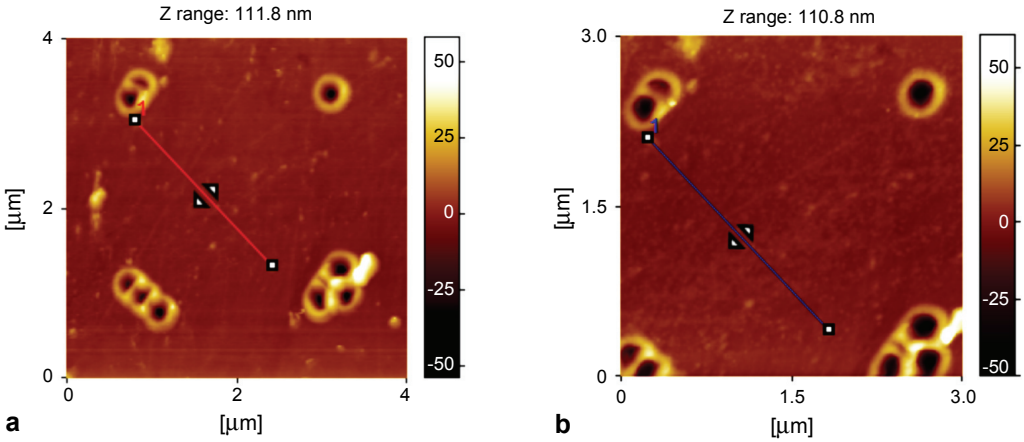

Fig. 4. To be continued on the next page.

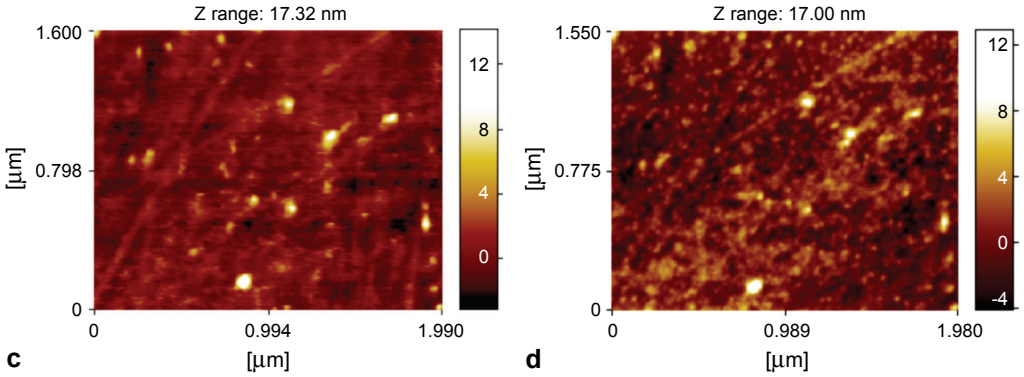

Fig. 4. The topography of the polycarbonate sample before (**a**, **c**) and after (**b**, **d**) the exposure. The surface roughness calculation presented in Tab. 1 was performed using (**c**, **d**) maps.

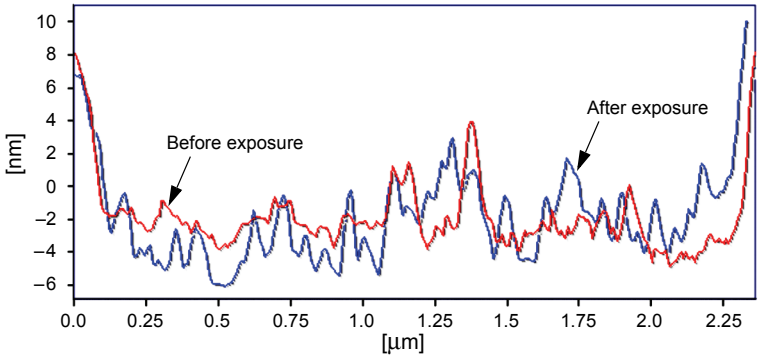

Fig. 5. The profiles of the polycarbonate surface before and after the exposure acquired along the lines presented in Figs. 4**a** and 4**b**.

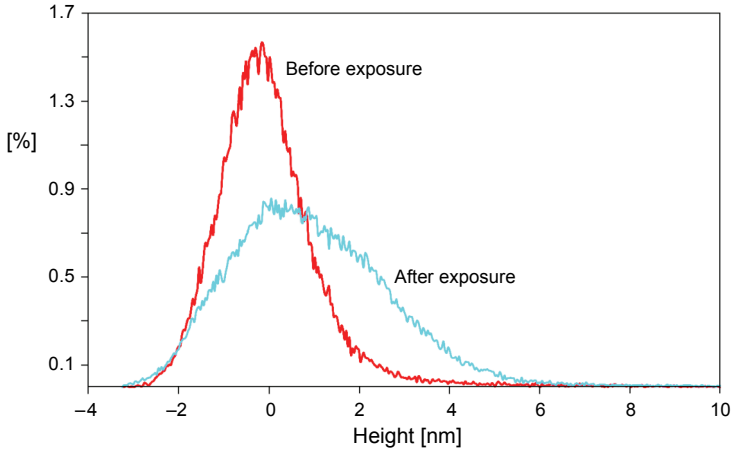

Fig. 6. The height distribution histograms of the polycarbonate sample before and after the UV light exposure calculated using data presented in Figs. 4**c** and 4**d**.

T a b l e 1. Selected roughness parameters of the polycarbonate sample before and after the UV light exposure [18].

Symbol	Parameter name and short description	Before exposure	After exposure	Unit
S_a	Roughness average	0.86	1.37	nm
S_q	Root mean square roughness	1.25	1.75	nm
S_{sk}	Surface skewness, describes the asymmetry of the height distribution histogram	2.332	0.887	–
S_{ku}	Surface kurtosis, describes the "peakedness" of the surface topography, and is defined	16.435	5.375	–
S_{ds}	Density of summits, is the number of local maximums per area	130.56	159.89	μm^{-2}
S_{dr}	Surface area ratio, expresses the increment of the interfacial surface area relative to the area of the projected (flat) *xy* plane	0.307	0.533	%
S_k	The core roughness depth, is the height difference between the intersection points of the found least mean square line	2.37	4.29	nm

Inner markers allowed to find easily the analyzed area (Fig. 4). The changes in the morphology are significant, therefore performing such measurement without nanomarkers could be difficult as recognizing this area would require a very careful analysis. Obtained data allowed to quantify the alteration of the surface. The profile lines and the area roughness analysis were presented in Figs. 5 and 6.

The profile roughness increase is easy to notice. The RMS value measured along the presented profiles (Fig. 5) are: 2.21 nm and 2.71 nm before and after the exposure, respectively. The height distribution histograms (Fig. 6) were calculated using extracted areas presented in Figs. 4**c** and 4**d**. Selected roughness parameters and calculated values are shown in Tab. 1.

A significant increase in the roughness of the polycarbonate surface due to UV light radiation was confirmed (S_a and S_q). Also the increase in the surface area ratio can be noticed. The asymmetry of the height distribution histogram (S_{sk}) decreased as both: peaks and hills became almost equally frequent on the surface. It is also indicated by the density of summits (S_{dr}) showing the increase in local maximums per area unit. Moreover, the peak of the histogram is not as narrow as before the exposure (S_{ku} decrease), which indicates the appearance of a number of new features on the surface.

It must be underlined that during the data processing, the blind reconstruction of the tip was performed in order to calculate the topography uncertainty map and to verify if the tip shape affected the imaging process and could have an impact on the final result. No significant issues were identified within the analyzed area.

Concerning the investigation of the certain conditions impact on the surface, the procedure involving surface imaging, nanomarkers development, sample exposure and verification imaging, can be performed according to the algorithm presented in Figure 7.

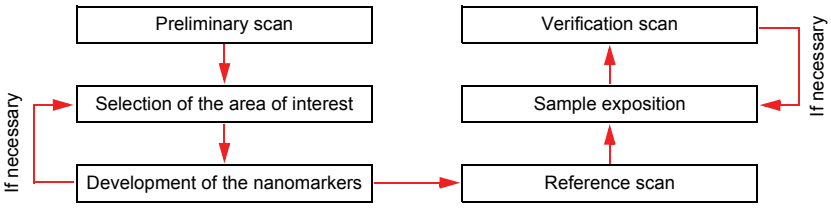

Fig. 7. The diagram illustrating the procedure of the nanomarkers development and utilization.

As the efficiency of developed procedure was presented, it can be utilized in the investigation of the topography alteration due to the impact of various conditions [5–8, 19].

4. Summary

In this paper, the development and the test of utilization of nanomarkers were presented. The nanoscratching technique was proposed as the most convenient method in terms of application of AFM in investigation of the morphology change due to environmental conditions. It was proven that the proposed approach allows to avoid time-consuming procedure of searching of a certain spot. The time necessary to perform the positioning of the AFM probe can be reduced to a few minutes. Obtained results are reliable, therefore the analysis of the influence of certain factors can be done with high confidence. During the test, the same area of the polycarbonate sample was measured and despite some morphology changes, it could be easily compared with high precision. The significant increase in the roughness due to UV light radiation was observed. Calculated roughness parameters can be compared with high confidence as they refer precisely to the same area of interest. It should be underlined that no such an approach was published yet.

The presented solution can be also used in observation of the surface properties with other AFM techniques such as EFM (electrostatic force microscopy), MFM (magnetic force microscopy), SThM (scanning thermal microscopy), where the morphology would remain unchanged. One needs to take into account the possibility of unwanted particles appearance as the result of nanoscratching process. In such a case, other nanomarkers pattern can be used in order to reduce the risk of the tip or surface contamination.

Acknowledgments – This work was performed within the frames of IEL statutory work. The author acknowledges his gratitude to Paweł Lochyński (Wrocław University of Technology, Poland) for providing the electropolished stainless steel sample.

References

[1] PN-EN 60068-2-5:2002 standard.
[2] PN-EN ISO 4892-2:2009/A1:2009 standard.
[3] PN-EN 60068-2-38:2010 standard.
[4] PN-EN 60068-2-14:2009 standard.

[5] SURESH B., MARUTHAMUTHU S., KHARE A., PALANISAMY N., MURALIDHARAN V.S., RAGUNATHAN R., KANNAN M., NAVANEETHA PANDIYARAJ K., *Influence of thermal oxidation on surface and thermo--mechanical properties of polyethylene*, Journal of Polymer Research **18**(6), 2011, pp. 2175–2184.
[6] NOWICKI M., RICHTER A., WOLF B., KACZMAREK H., *Nanoscale mechanical properties of polymers irradiated by UV*, Polymer **44**(21), 2003, pp. 6599–6606.
[7] CANETTA E., MONTIEL K., ADYA A.K., *Morphological changes in textile fibres exposed to environmental stresses: Atomic force microscopic examination*, Forensic Science International **191**(1–3), 2009, pp. 6–14.
[8] ROBERTSON C., WERTHEIMER M.R., FOURNIER D., LAMARRE L., *Study on the morphology of XLPE power cable by means of atomic force microscopy*, IEEE Transactions on Dielectrics and Electrical Insulation **3**(2), 1996, pp. 283–288.
[9] RITTER M., DZIOMBA T., KRANZMANN A., KOENDERS L., *A landmark-based 3D calibration strategy for SPM*, Measurement Science and Technology **18**(2), 2007, pp. 404–414.
[10] SANTINACCI L., DJENIZIAN T., SCHMUKI P., *Nanoscale patterning of Si(100) surfaces by scratching through the native oxide layer using atomic force microscope*, Applied Physics Letters **79**(12), 2001, pp. 1882–1884.
[11] RAMIĄCZEK-KRASOWSKA M., PRAŻMOWSKA J., LOS K., STAFINIAK A., SZYSZKA A., PASZKIEWICZ R., ORSKI W., TARNOWSKI K., TŁACZAŁA M., *Creation of high resolution pattern by nanoscratching*, Central European Journal of Physics **9**(2), 2011, pp. 404–409.
[12] KAKIAGE M., ICHIKAWA T., YAMANOBE T., UEHARA H., SAWAI D., *Structure and property gradation from surface to bulk of poly(L-lactic acid)/poly(D-lactic acid) blended films as estimated from nanoscratch tests using scanning probe microscopy*, ACS Applied Materials and Interfaces **2**(3), 2010, pp. 633–638.
[13] TURRI S., TORLAJ L., PICCININI F., LEVI M., *Abrasion and nanoscratch in nanostructured epoxy coatings*, Journal of Applied Polymer Science **118**(3), 2010, pp. 1720–1727.
[14] TSENG A.A., SHIRAKASHI J.-I., NISHIMURA S., MIYASHITA K., ZHUANG LI, *Nanomachining of permalloy for fabricating nanoscale ferromagnetic structures using atomic force microscopy*, Journal of Nanoscience and Nanotechnology **10**(1), 2010, pp. 456–466.
[15] ZHANG HUA-LI, KUAI JI-CAI, ZHANG FEI-HU, *Minimum thickness of cut in nanomachining using atomic force microscopy*, 2010 International Conference on E-Product E-Service and E-Entertainment (ICEEE), 2010.
[16] JANG K., ISHIBASHI Y., IWATA D., SUGANUMA H., YAMADA T., TAKEMURA Y., *Fabrication of ferromagnetic nanoconstriction using atomic force microscopy nanoscratching*, Journal of Nanoscience and Nanotechnology **11**(12), 2011, pp. 10945–10948.
[17] JEN-CHING HUANG, CHIA-LIN LI, JYH-WEI LEE, *The study of nanoscratch and nanomachining on hard multilayer thin films using atomic force microscope*, Scanning **34**(1), 2012, pp. 51–59.
[18] http://www.imagemet.com/WebHelp/spip.htm#roughness.htm, accessed 05.05.2012.
[19] SIERAKOWSKI A., JANUS P., KOPIEC D., NIERADKA K., DOMANSKI K., GRABIEC P., GOTSZALK T., *Optimization method of photolithography process by means of atomic force microscopy*, Proceedings of SPIE – The International Society for Optical Engineering **8352**, 2012, article 83520B.

Received May 25, 2012
in revised form November 7, 2012