KSTLE International Journal, Vol. 1, No. 2, December 2000, pp. 69-75

Phase Imaging of Worn Surface of TiN Coating and Interpretation by Force Spectroscopy

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Abstract : The paper compares topography, phase contrast and force spectroscopy in atomic force microscopy data for evaluating the microheterogeneity of surface layer. The worn surface of ion-plated TiN coating was measured using both a laboratory-built and a commercial AFM. The results of analysis revealed structural and micromechanical heterogeneity of the worn surfaces. We demonstrated that the phase image allows relatively qualitative estimation of elastic modulus of the sample surface. The tribolayer formed in the worn surface possessed much lower stiffness than the original coating. It is shown that the most stable phase imaging is provided with a stiff cantilever. In this case, phase contrast is well conditioned, first of all, by microheterogeneity of elastic properties of the investigated surfaces. In this study, an attempt was also made to correlate the results of phase imaging with that of the force spectroscopy. The joint analysis of information on the surface properties obtained by the phase imaging and quantitative data measured with the force spectroscopy methods allows a better understanding of the nature of the surface micromechanical heterogeneity.

Keywords : atomic force microscope, phase imaging, force spectroscopy, worn surface, TiN coating

Introduction

The atomic force microscope (AFM) is a complex instrument used to investigate a surface on a micro- and nano-scale. Various modes of scanning are applicable in the AFM depending on the purpose of measurement. The basic modes are contact mode, non-contact mode and intermittent contact mode. In contact mode, the probe tip is located at the end of a soft cantilever and slides on a surface of a sample surface with an extremely small load (down to 10^{-10} N) [1,2]. The height of the fixed end of the cantilever relative to the surface is typically adjusted with feedback to maintain the bending at a predetermined amount during lateral scanning in horizontal plane. The adjustment amount with respect to the lateral position produces a map of surface topography. The image of lateral force (friction force) of the probe against the sample surface can also be obtained. In non-contact mode, the cantilever with a probe tip vibrates at a small amplitude at close proximity to a surface such that attractive force between the tip and sample surface is sensed [3]. Typically the vibration amplitude of the cantilever provides a feedback signal that allows the tip-sample spacing to be held constant for profiling applications. In intermittent contact mode (or tapping mode), a cantilever is forced to vibrate with amplitude at its resonance frequency in the absence of tipsample interaction. Such an oscillating cantilever is then brought close to a sample surface so as to make it tap the surface with a set-point amplitude smaller than the free amplitude. This set-point amplitude is kept constant during scanning by the feedback mechanism [4]. With the intermittent contact mode, inelastic surface deformation is minimized as a result of short duration of the contact between the probe and the sample surface. In each oscillation cycle, the probe tip touches directly the sample surface for a short period of time during which it experiences intermolecular attraction and repulsion. Even with such a short contact time, a variation of important parameters such as amplitude, frequency, and phase shift occurs, and monitoring of these parameters can be used for retrieving information of the local microheterogeneity of the sample surface layers. In particular, the phase shift of cantilever oscillation can be measured and used for phase imaging.

The phase imaging is sensitive to variations in local material properties and hence has become an important tool for surface analysis [5-8]. Several works have reported the application of phase images for estimating structural heterogeneity of materials [9-16]. It was shown, for instance, that the phase shift depends on the material stiffness [7,9,10]. The phase image, however, does not provide quantitative information about the micromechanical properties of the surface.

Force spectroscopy enables to quanitatively characterize surface force (adhesion) and local micro-mechanical properties such as elastic modulus of a thin surface layer of materials, by recording the deflection of the cantilever as the tip approaches and retracts from a sample surface (force-distance curve) [17,18]. Force Volume Image [19] can then be constructed by

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obtaining a set of force vs. distance curves over a scanned area. Therefore the combined use of phase image and force spectroscopy is much more effective for characterizing microheterogeneity of the surface layer.

In the present work we demonstrated the significance of phase shift and force spectroscopy information of the atomic force microscopy for characterizing the tribolayer formed on the worn surface of TiN coating. Theoretical description of the phase shift mechanism for oscillating probe under the influence of various factors is quite complex. Therefore, we used experimental approach in this investigation.

Experimentation

Specimen and test conditions

The TiN coating used for this study was deposited by ion plating method using a multi-arc process. The heat-treated EN31 steel discs (126 mm diameter, 10 mm thick.) were ground and lapped to ensure a high quality surface finish (~0.05 μm Ra). The disc specimens were degreased in 111-trichloroethene, vapor blasted using 400 grit Al_2O_3 media, ultrasonically cleaned and rinsed with water in a detergent bath. To remove surface contamination, the specimens were bombarded by the highly energized Ti ions produced in the discharge by evaporating the titanium sources using arc sources. The bias voltage was -1000 V and pressure was dropped to 1×10^{-6} Torr. For deposition of TiN, high purity nitrogen gas (99.999%) was backfilled to a pressure of 8×10^{-3} Torr and the bias voltage was reduced to -150 V. Titanium sources were evaporated into the discharge and deposited on the specimen surface for 2 hours. The thickness of the coating (measured by the X-ray fluorescence technique) was approximately 3 mm and the effective hardness, measured by the Vickers Hardness Tester, was around 710 Hv.

A roller-on-disc wear tester was used at room temperature in a laboratory environment. Bearing rollers (FAG), 6 mm in diameter and 5.3 mm in length and hardness of 800-850 Hv, were used as stationary specimens. The surface roughness of the TiN coating was in the range 0.13-0.2 μm Ra and that of the roller was 0.1 μm Ra in axial direction and 0.015 μm Ra in circumferential direction. The TiN coated disc specimen was rotating with a linear velocity of 1.0 m/s against the stationary steel roller for 10^4 revolutions. The applied contact load was 80 N.

Surface characterization

Measurement of topography and phase shift was carried out using a laboratory-built AFM and the Nanoscope Dimension 3000. The former operates using a L-shaped tungsten probe with very high spring constant (or force constant, k_o= 380 N/m), while the latter operates using a commercial, V-shaped silicon nitride cantilever having a high spring constant (k_o= 96 N/m). Force spectroscopy analysis was conducted with the Nanoscope Dimension 3000 to evaluate the variation of elastic modulus and influence of contact adhesion on the tip-sample interaction. In the laboratory-built AFM, the oscillation of the probe was detected using an optical fiber interferometer. The L-shaped probe was fabricated from a tungsten wire (100 mm diameter) by electrochemical etching. Following parameters were used for the tungsten probe installed in our laboratory-built AFM: R= 100 nm (radius of curvature measured using the standard test sample TGT01 supplied by NT-MDT), ω_o= 44.9 kHz (operating frequency), Q_o= 166 (quality factor), A_o= 20 nm (free oscillation amplitude) and A_{sp}= 10 nm (set-point amplitude). The parameters used for the Nanoscope Dimension 3000 were: R = 42 nm, ω_o= 183 kHz , Q_o= 140, A_o = 80 nm and A_{sp}= 50 nm. It should be noted that currently available commercial probes, which have spring constant less than 100 N/m, do not allow obtaining sufficiently good phase contrast for stiff materials such as ceramics and hard coatings. On the other hand, the cantilevers having high stiffness are known to be effective for stiff materials and for complex surfaces in which wide variation of stiffness exists. To interpret the results of force spectroscopy, a set of force vs. distance curves over a scan area, called a Force Volume Image, was obtained and local value of elastic modulus was calculated based on the indentation load vs. penetration depth relationship [18].

Results and Discussion

Fig. 1 shows the topography and phase images of both initial and worn surface of TiN coating. The topography images contain morphologically characteristic features. The topography images showed that TiN coating surface after the wear test became slightly smoother than prior to the wear test. In comparison with the initial topography, the sliding friction resulted in smoothening of the surface. The analysis of the phase images provides more insight. The grey level of a location in the phase image is dependent on the elastic modulus of the surface and also possibly on the adhesion between the tip and the sample. However, the force-distance curves obtained for this sample using a cantilever having very high spring constant (~100 N/m) revealed very low influence of the adhesion on the tip-surface interaction. The influence of adhesion on the phase images which were obtained in this study using a cantilever having extremely higher spring constant (~380 N/m) can thus be neglected. The results of force-distance curve measurement will be explained in the latter part of this section (see Fig. 4). Therefore, the phase image in Fig. 1(d) revealed that the worn surface possessed ununiform micromechanical properties (microheterogeneity).

To obtain stable phase images of the studied material (stiff material), the use of proper probe is of great importance. As for the Nanoscope instrument, the commercial probes that have the spring constant in the range of 1~0.1 N/m did not produce phase images with a sufficient resolution. Even with the probes with maximum commercially available spring constant (NT-MDT microprobes with the cantilever spring constant ~96 N/m), the phase images were not so good as those obtained with our laboratory-built AFM, which employed a tungsten probe having a very high force constant. In other words, phase contrast of the stiff material surface was very weak when a softer cantilever is used. Fig. 2 illustrates the influence of the

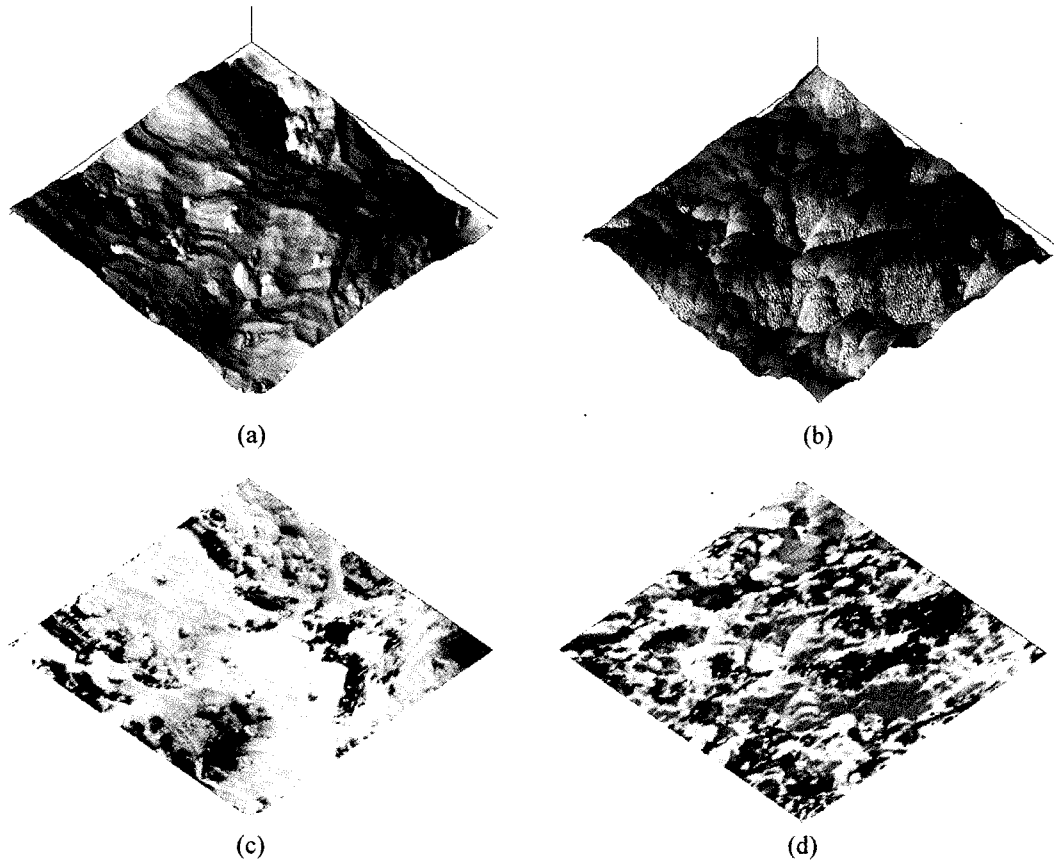

Fig. 1. Images of TiN coating surface obtained with the laboratory-built AFM. (a) topography and (c) phase image of the original surface of TiN coating (scan area = 9.4 × 9.4 μm, height amplitude = 582 nm, rms roughness = 79.8 nm, max. phase shift = 131.6°); (b) topography and (d) phase image of the worn surface (scan area = 9.4 × 9.4 μm, height amplitude = 365 nm, rms roughness = 65.6 nm, max. phase shift = 136.6°).

spring constant of the probes on the AFM images. The topography and phase images obtained using the very stiff cantilever (380 N/m) and using the less stiff cantilever (96 N/m) are shown in the left and right column, respectively. The images of topography, phase contrast and combined images of these two are shown in the first, middle and bottom row, respectively. The combined images were obtained by the summation of the topography and phase contrast AFM-matrices and showed the distribution of the material heterogeneity over the surface asperities. It was noted in our measurement that the scanning using the Nanoscope Dimension 3000 with a soft cantilever was less stable, causing defects in the images. In the regions, where very small shift of phase (black color in Fig. 3(e)) was observed, the image of topography also contained artifacts (Fig. 3(d)). It may be explained by the complexity of the choice of scanning parameters. In case where a scan area possessed markedly varied micromechanical properties, the soft cantilever seemed to cause an unstable scan results. The black regions in the topography and phase images (Fig. 2(d) and (e)) were due to the scan error, not representing any surface features. The images obtained with a stiff cantilever (very high force constant), Fig. 2(b), showed much wider grey level separation, corresponding to the variation of microstructural features of the worn surface. Therefore, the use of a probe having very high spring constant is beneficial to understand the variation of the surface features in the worn surface of stiff TiN coating. The high contrast in the phase images (Fig. 2(b) suggested that the surface possessed significantly different properties depending on the region. Distinct grey level separations in the phase image, which can be called as surface elastic modulus or stiffness map [10], enables to correlate each grey value with a specific elastic modulus or stiffness. The phase image of the worn surface showed mainly three types of locations with different grey levels; bright, dark grey and black. The regions corresponded to dark grey and black were attributed to lower stifness of the surface layer (tribolayer) formed in the worn surface; the darker the grey level, the lower the stiffness of the surface. A possible source of this grey level contrast is the localized transfer of materials from the softer steel ball to the harder TiN coating. It should also be noted that the combined image of topography and phase contrast, as shown in Fig. 2(c), helps to understand the relationship between the topographical surface features, such as summits and valleys, and variation of surface stiffness as represented by different grey scales.

To quantitatively evaluate the above scan results, force spectroscopy analysis was followed using the advanced function of the Nanoscope Dimension 3000. Fig. 3(a) and (b)

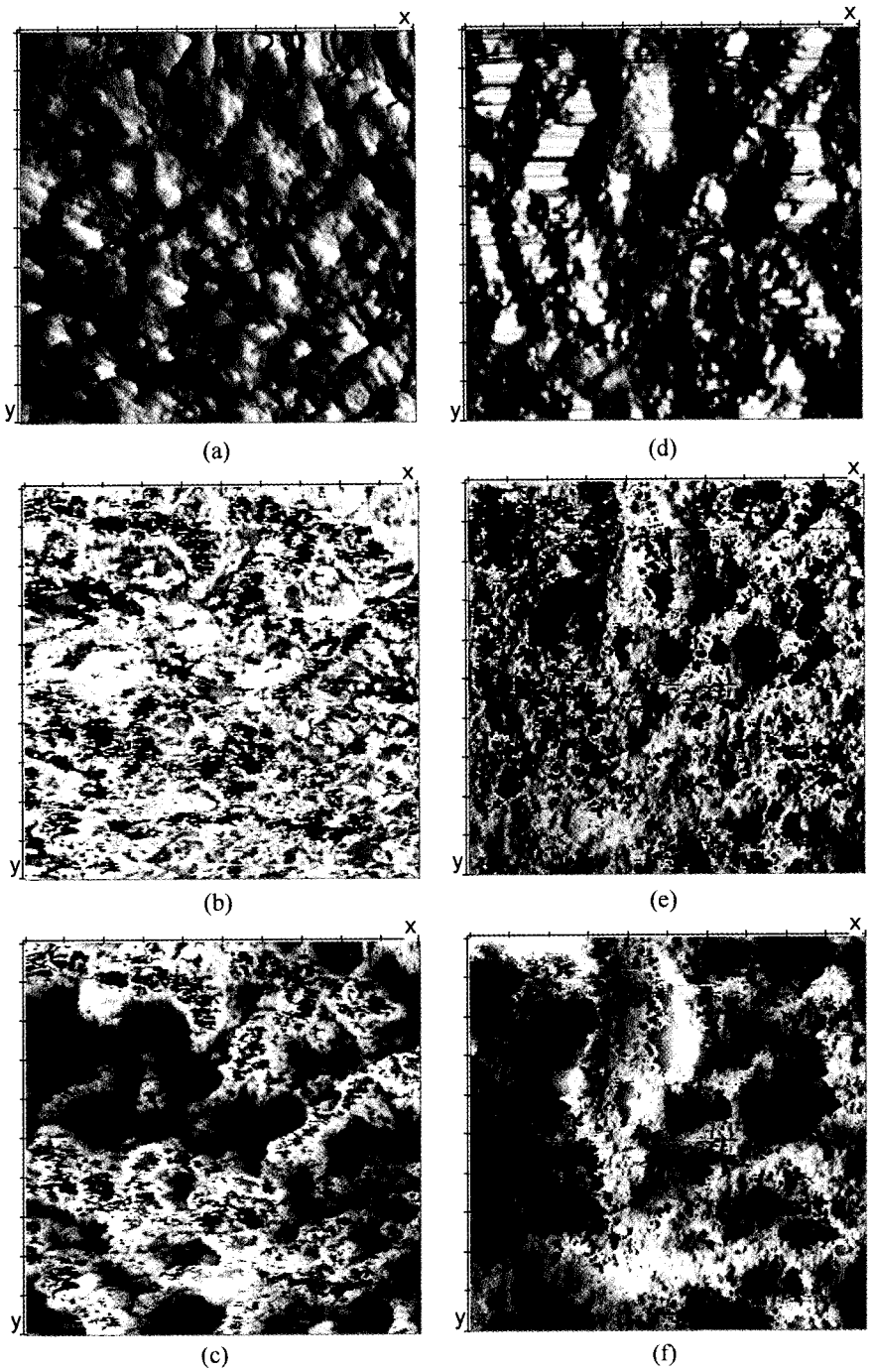

Fig. 2. Comparative analysis of AFM-data for the worn surface of TiN coating. (a)~(c) data obtained with the laboratory-built AFM (scan area = 19 × 19 μm; height amplitude = 446 nm; max. phase shift = 146°; (d)~(f) data obtained with Nanoscope Dimension 3000 (scan area = 20 × 20 μm; height amplitude = 620 nm; max. phase shift = 140°; (a), (d) topography; (b), (e) phase images; (c), (f) combined images.

show the images of topography and phase shift of the worn surface of TiN coating obtained with the commercial cantilever having lower stiffness (~96 N/m), respectively. Although the images were not so clear as those we showed earlier, one can note that there were three discernable regions having different contrast in the phase image as marked with the letter A, B and C in Fig. 3(b). The Force Volume Image was obtained for the same areas and presented in Fig. 3(c). Due to the large time consumption for the imaging in Force Volume mode, the data matrix size for the force spectroscopy was restricted to 32 × 32. Nevertheless, one can note a good correlation between the height representation of the force spectroscopy data (Fig. 3(c)) and the phase image (Fig. 3(b)). The pull-off region in the retracing curves, as marked with an arrow in Fig. 4(a) and (b), indicated that there was similar amount influence of adhesion interaction between the tip and the surface at the

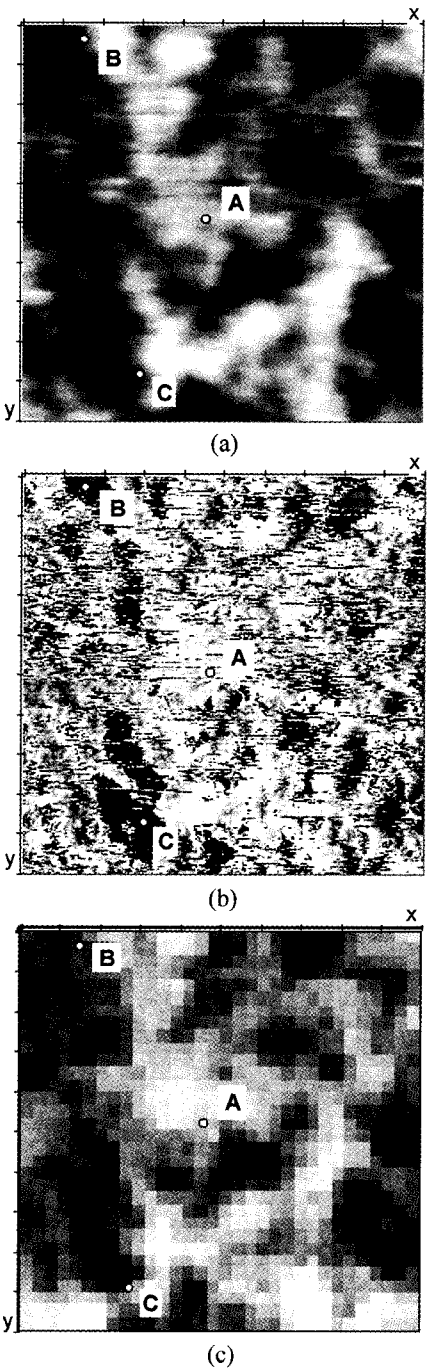

Fig. 3. (a) topography, (b) phase and (c) force spectroscopy images of TiN worn surface (scan area = 20 × 20 μm; height amplitude = 997 nm; max. phase shift = 152°).

positions A and B but the position B. However, the phase image (Fig. 3(b)) showed that the positions A and B experienced conspicuously different amount of phase shift. Therefore, it is conceivable that adhesive force did not significantly influence the phase shift of the oscillating probe. By contrast, Fig. 4(c) showed negligible adhesion force at the position C. Therefore, adhesive force could not significantly influence the phase shift of the oscillating probe and, accordingly, the phase shift was mainly governed by the surface elastic properties in the analyzed regions. The analysis of the force vs. distance curves was then conducted for the selected points corresponding to the three different zones in the phase image. Fig. 4 shows the results of the force-distance curve analysis (left plots) together with the corresponding dependencies of the probe penetration on the applied load (right plots; penetration depth vs. indentation load). In the penetration depth vs. indentation load curves, the solid and dotted lines represented indentation depth and its 3/2 power, respectively. In the Hertzian circular contact between two elastic materials, the indentation load is proportional to the 3/2 power of the indentation depth. However, the right plots in Fig. 4(b) and (c) showed that the relationship between 3/2 power of penetration depth and indentation load is not linear. This non-Hertzian contact behavior is often observed with a soft layer on a hard substrate. The thickness of the tribolayer at position B was approximately 38 nm and at position C, about 82 nm. The plots of probe penetration depth vs. indentation load enabled rough estimation of the material elastic modulus in the measured positions based on Hertz theory [18]. For the position A (Fig. 4(a)), however, it was unable to calculate the elastic modulus as the surface as this position was too stiff to be indented with the commercial silicon nitride tip used in this study. During the measurement, the cantilever deflected but there were no penetration of the tip into the material. For two other positions, B (Fig. 4(b)) and C (Fig. 4(c)), Youngs modulus were calculated as 4.75 and 0.62 GPa, respectively, based on the simple assumption of linear relationship between penetration depth and indentation load as illustrated in the plots. These values are much less than the Youngs modulus value of conventional physically vapor deposited TiN coating (300~400 GPa). The calculated values are rather close to that of rigid polymers, revealing the organic nature of the tribolayers.

Conclusions

In this study, we demonstrated that the phase image allows relative qualitative estimation of micromechanical properties of the sample surface. An attempt was then made to correlate the results of phase imaging with that of the force spectroscopy. The use of phase imaging and force spectroscopy for investigating the worn surfaces of TiN coating has led to following conclusions.

1. Significant heterogeneity of the worn surfaces was identified by the difference in grey levels in the phase mages.
2. The tribolayer and/or layer, formed by material transfer of counterfacing steel ball, possessed much lower stiffness than the original coating.
3. The joint analysis of information on the surface properties obtained by the phase imaging and quantitative data measured from the force spectroscopy methods allows a better understanding of the nature of the surface micromechanical heterogeneity.
4. However, such analysis demands optimal choice of the probe with spring constant corresponding to the

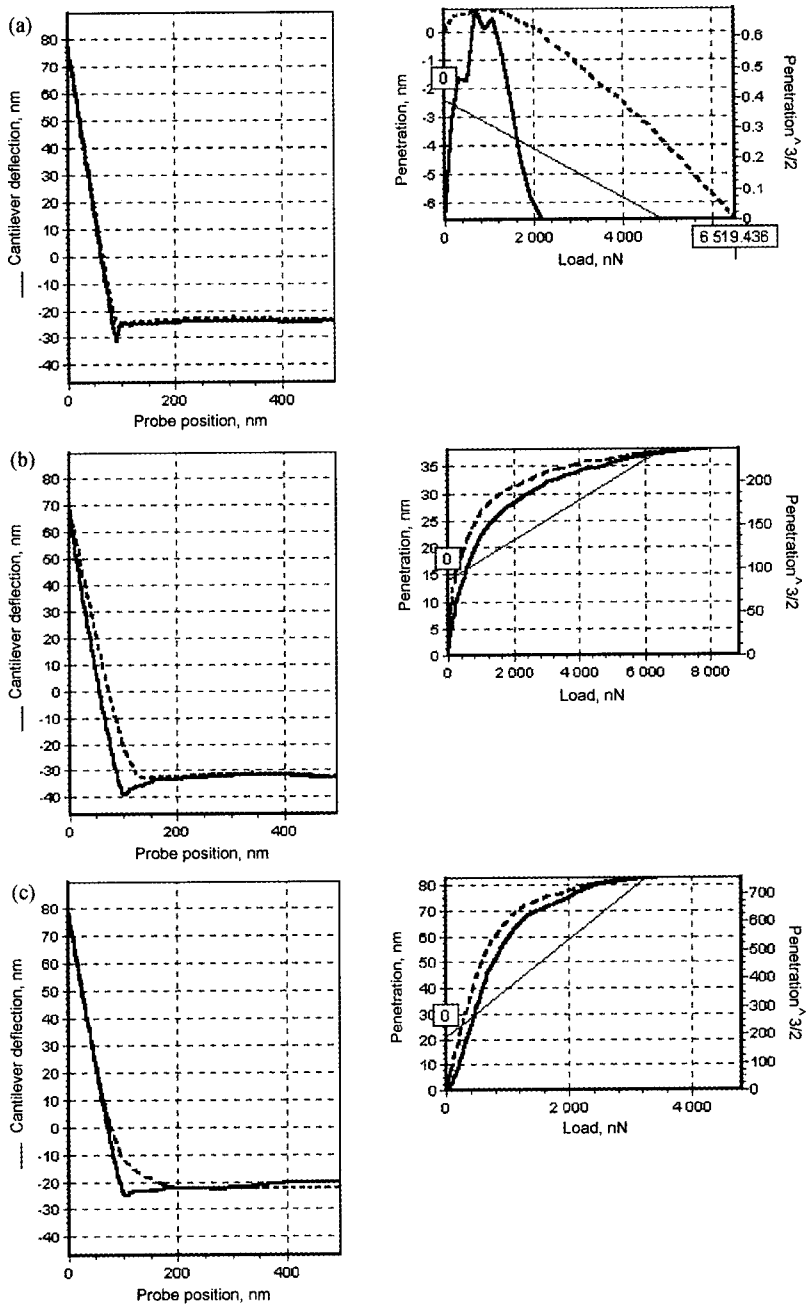

Fig. 4. Results of Force Volume analysis for the worn of TiN coating for selected positions as marked in Fig. 3; (a), (b) and (c) force spectroscopy for the local regions A, B and C as shown in Fig.3, respectively. Dotted and solid line in the left plots indicate the approaching and retracting of the probe. Solid and dotted line in the right plots indicate indentation depth and its 3/2 power, respectively.

investigated material stiffness and supposed difference in stiffness over the sample.

Acknowledgment

Support for this work by the Ministry of Science and Technology through the National Research Laboratory Program is gratefully acknowledged. The authors thank V. Tsukruk, and V. Gorbunov (Materials Science and Engineering Department, Iowa State University) for the measurement of force-distance curve and useful discussion about the influence of adhesion on the tip-sample interaction.

References

1. O. Marti, Nanotribology: friction on a nanometer scale, Physica Scripta T49, 599-604, 1993.
2. M. Bingelli and C. M. Mate, Influence of capillary condensation of water on nanotribology studied by force microscopy, Appl.Phys. Lett. 65, 415-417, 1994.

3. Y. Martin, C. C. Williamson, and H.K. Wickramasinghe, Atomic force microscope Force mapping and profiling on a sub 100-A° scale, Journal of Applied Physics, vol. 61, No. 10., 4723-4792, 1987.
4. Zhong Q., Inniss D., Kjoller K., Elings V. B., Fractured polymer/silica fiber surface studied by tapping mode atomic force microscopy, Surf. Sci. Lett. 290, L688-92, 1993.
5. B. Anczukowski, D. Krüger and H. Fuchs, Cantilever dynamics in quasinoncontact force microscopy: Spectroscopic aspects , Phys. Rev. B 53, 15485-15488, 1996.
6. R.G. Winkler, J.P. Spatz, S. Sheiko, M. Mõller, P. Reineker and O. Marti, Imaging material properties by resonant tapping-force microscopy: A model investigation, Phys. Rev. B54, 8908-8912, 1996.
7. S.N. Magonov, V. Elings and M.-H. Whangbo, Phase imaging and stiffness in tapping-mode atomic force microscopy, Surf. Sci. Lett. 375, L385-391, 1997.
8. J. Tamayo and R. Garcßa, Effects of elastic interactions on phase contrast images in tapping-mode scanning force microscopy, Appl. Phys. Lett. 72, 2394-2396, 1997.
9. H.-S. Ahn, S. A. Chizhik and A. M. Dubravin, Atomic force microscopy of TiN friction surface, J. of Friction and Wear, Vol. 20, 3544, 1999.
10. H.-S. Ahn, S.A. Chizhik, Characterization of wear surfaces using phase imaging in atomic force microscopy, Submitted to J. of Tribology(ASME), 2000.
11. S. N. Magonov, J. Cleveland, V. Elings, D. Denley and M.-H. Whangbo, Tapping-mode atomic force microscopy study of the near-surface composition of a styrene-butadiene-styrene triblock copolymer film, Surf. Sci., Vol. 389, 201-211, 1997.
12. G. Haugstadt and R. R. Jones, Mechanisms of dynamic force microscopy on polyvinyl alcohol: region-specific non-contact and intermittent contact regimes, Ultramicroscopy, Vol. 76, 77-86, 1999.
13. H. G. Hansma, K. J. Kim and D. E. Laney, Properties of biomolecules measured from atomic force microscope images: a review, J. Str. Biol., Vol. 119, 99-108,1997.
14. I. Schmitz, M. Schreiner, G. Friedbacher and M. Grasserbauer, Phase imaging as an extension to tapping mode AFM for the identification of material properties on humidity-sensitive surfaces, Appl. Surf. Sci., Vol. 115, 190-198, 1997.
15. K. A. Ramirez-Aguilar, D. W. Lehmpuhl, A. E. Michael, J. W. Birks and K.L. Rowlen, Atomic force microscopy for analysis of environmental particles, Ultramicroscopy, Vol. 77, 187-194, 1999.
16. M. W. Nelson, P. G. Schroeder, R. Schlaf and B. A. Parkinson, Two-dimensional dopant profiling of patterned Si wafers using phase imaging tapping mode atomic force microscopy with applied biases, J.Vac.Sci. and Technol. B, Vol. 17, 1354-1360, 1999.
17. N. Burnham and R. J. Colton, Measuring the nanomechanical properties and surface forces of materials using an atomic force microscope, J. Vac. Sci. and Technol. A, Vol. 7, 2906-2913, 1989.
18. S. A. Chizhik, Z. Huang, V. V. Gorbunov, N. K. Myshkin and V. V. Tsukruk, Micromechanical properties of elastic polymeric materials as probed by scanning force microscopy, Langmuir, Vol. 14, 3012-3015, 1998.
19. W. F. Heinz, E. A. Hassan, J. A. Hoh, Applications of Force Volume Imaging with the Nanoscope Atomic Force Microscope, Technical Brochure, Digital Instruments.