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Mechanical Nanoprocessing and Nanoviscoelasticity of Surface-Modified Polycarbonate

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Additional information is available at the end of the chapter

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Abstract

To clarify their potential as atomic force microscope (AFM) memory media, the nanometer-scale mechanical processing properties of untreated and fluorocarbon plasma-treated polycarbonate samples were determined via the sliding of an AFM tip. The surface energy of the polycarbonate was reduced by the fluorocarbon plasma treatment, as well as the force necessary for processing. Nanometer-scale precise processing of the polycarbonate was realized after the fluorocarbon plasma treatment, and the interval pitch in the formation of lines, spaces, and nanometer-scale fine dots was minimized to 60 nm with these samples. The viscoelastic properties of the fluorinated polycarbonate were evaluated using an AFM in force modulation mode. The fluorocarbon plasma treatment reduced the friction force of the polycarbonate sample and improved its wear resistance, which caused the friction durability corresponding to the reliability of data reproduction to be markedly improved. These results show that high-density recording can be realized by nanometer-scale processing of fluorocarbon plasma-treated polycarbonate samples.

Keywords: nanometer-scale processing, viscoelasticity, atomic force microscopy, polycarbonate, fluorocarbon plasma treatment, high-density memory

1. Introduction

Based on the application of scanning probe microscopy in nanoprocessing technologies, mechanical nanoprocessing technology at the atomic scale is attracting great attention for nanomachines and nanodevices. Scanning tunneling microscopy and related techniques are promising for the development of the manufacture of atomic-scale writing by means of tip

scanning using a piezoelectric element [1]. In nanoprocessing, the semiconductor manufacturing process comprising etching, deposition, and lithography has mainly been applied. In future nanotechnology processes, however, it is expected that various machine elements such as bearings and sliders will be manufactured by manipulating atoms or molecules. On the one hand, microtribology has been studied using atomic force microscopy (AFM), whereby tribological processing is performed by scanning the AFM tip on a sample surface. On the other hand, wear tests have been carried out on diamond-like carbon (DLC), ion-implanted DLC, and cubic boron nitride films [2–4] whereupon a $1 \times 1 \mu\text{m}^2$ square with a depth of 5–10 nm was formed by wearing and the maximum roughness depth at the bottom of a processed groove was about 1 nm [3].

The atomic wear of a material with a layered crystal structure has been evaluated in previous studies based on the topographic changes that occur because of sliding. Materials with layered crystal structures such as muscovite mica have basal planes that interact weakly, so the surface of these materials is easily cleaved and can be observed on the atomic scale. Wear on the mica surface mainly occurs to a depth of about 1 nm, which corresponds to the distance from one cleavage plane surface to the one immediately beneath it [4]. By exploiting this wear mechanism, high-precision processing can be performed whose units correspond to the period of the layers in a multilayered crystal material that has periodic weak van der Waals bonds [5]. Processing begins at a certain critical load, and the processing depth increases discretely with the load. Fracture easily occurs at the two cleavage planes of the SiO_4 -K and K- SiO_4 interfaces of muscovite mica, upon which 1- and 0.8-nm-deep mechanical processing has been performed by AFM in a previous study [6]. Because the processing of nanometer-scale shapes to a layer-period unit depth is possible, the mechanical processing of the standard ruler and the application to high-density recording technology has been proposed [7, 8]. To test the molecular bearing supported by the van der Waals force, a nanometer-scale slider has been proposed by applying AFM mechanical processing. Very fine dots composed of clusters of atoms supported by the van der Waals force were processed, called nanosliders, and the movement of these nanosliders has subsequently been evaluated [9, 10].

Polymer storage media play a crucial role in storage systems, and polycarbonate (PC) has attracted great attention as an AFM memory media. Although PC materials have been applied to light discs in large-scale applications owing to their smooth surface property and low cost, line-scratched PC surfaces exhibit plastic deformations at the nanometer scale [11] because PC has a low mechanical strength and a high molecular weight. In this way, the plastic deformation causes the development of large-sized surface damage and wear when attempting fine processing and reproduction at low loads. Furthermore, PC lacks wear-resistant properties to prevent the development of deformations. However, when considering their microtribological properties, polymer materials easily generate the deformation of lumps in thermal processing and typically have an inferior wear-resistant property. Because PC lacks wear resistance, a head-disc system made with this material is easily damaged owing to the contact between the head and the tip. Therefore, various protective films have been prepared to cover these materials.

Presently, the application of PC materials for pit fabrication, reproduction, and ultrahigh-density recording is being investigated [12] using the fabrication and formation techniques of field evaporation and electron kinetic energy [13–15]. In field evaporation, a voltage is applied between the probe and the substrate, causing local heating and evaporation to occur. This evaporation makes it possible to remove and deposit an individual atom or a cluster, while the heating creates fine holes on the surface and changes the electronic properties of the surface [13–15]. If this heating technique was applied to a PC substrate for ultrahigh-density recording by AFM, these effects are expected to enable fabrication of very fine patterns and to permit recording densities of more than 60 Gbits/in². Polycarbonate substrates, therefore, are a promising material for Millipede memory recordings that combine ultrahigh density, terabit capacity, a small form factor, and a high data rate.

The facilitation and precision of micromachining are indispensable to media recording, and this high-precision recording at the nanometer scale must be performed at a high speed. In addition, it is important to reproduce recording marks by tip scanning without inducing any change via surface deformation of the media; that is, it is necessary to control surface wear deformation at the nanometer scale. It is known that a contact start/stop cycle during recording operation is influenced by the micromachining stiction, which is that occurs between the head and the media. The capillary condensation of liquids from vapor, and especially water, can have additional effects upon the whole physical state of the contact zone, so the effect of absorbed water upon the tribological properties of the media surface is considered. For example, if the surfaces contain adhesive water molecules, these will increase the frictional force and atomic force between the tip and media surface. Conversely, this absorbed water also acts as a protective lubricating film on the media. It is difficult to control the effects of the absorbed water upon the recording, which can be reproduced using an AFM tip at a low load, and the absorbed water results in accidental errors in the recording because of water adhesion between the tip and media. For these reasons, it has been proposed to process the DLC film using a fluorocarbon plasma treatment and to characterize and optimize the treated film to improve its wear properties. However, PC materials are a promising ideal medium that should be easily deformable for bit writing, and yet the writing bits should be stable against tip wear and thermal degradation. It has also been proposed to treat the PC specimens with fluorocarbon plasma and subsequently coat them with an ultrathin DLC film. The surface-free energy of these modified PC specimens is thereby reduced and the interaction between the head and medium is thus decreased, which enables fine nanoprocessing to be realized.

In this study, to realize high-density memory based on PC materials as a recording media and exploit its unique tribological and viscoelastic properties, PC specimens were subjected to fluorocarbon plasma treatment. The untreated polycarbonate (untreated PC) and fluorocarbon plasma-treated polycarbonate (CF₄-treated PC) samples were characterized by measuring the surface-free energy, nanoindentation hardness, and the wear properties using the liquid-drop method and AFM techniques. High-density recording was realized by nanometer-scale processing of the untreated and CF₄-treated PC samples, and the processing properties of these samples were evaluated and characterized.

2. Experimental methods

2.1. Sample preparation

Polycarbonate was used as specimens in our study. A PC sample was treated by radio frequency (RF) magnetron sputtering with carbon tetrafluoride (CF_4) gas. The PC sample surface was subjected to a high-frequency (13.56 MHz) voltage for fluorocarbon plasma treatment. All experiments have been described elsewhere [16]. The experiments were performed under the conditions of an RF power of 0.25 W on the sample, a bias voltage of 0.8 kV, a vacuum pressure of 2×10^{-2} Torr, and a sputtering time of 30 min [16]. To investigate the effect of fluorocarbon plasma on PC samples, liquid-drop method was used to measure the surface-free energy of the samples [16]. A shape of a liquid drop deposited on the sample surface was evaluated to measure the contact angle between the drop and the surface, from which the surface-free energy was obtained based on the extended Fowkes theory of Ref. [3]. Drops of refined water, methyl iodide, and n-hexadecane were used in this study, and the hydrophobicity of these drops was determined by the contact angle of the droplet to the specimen surface. The surface-free energy (γ_s) is given by the sum of the dispersion force (γ_{sd}), the dipole force (γ_{sp}), and the hydrogen bond (γ_{sh}), such that

$$\gamma_s = \gamma_{sd} + \gamma_{sp} + \gamma_{sh}. \quad (1)$$

2.2. Nanoindentation evaluation

To study the mechanical properties of untreated and CF_4 -treated PC samples, an AFM in combination with a dynamic stiffness measurement system (Digital Instruments Nanoscope III, Hysitron Inc.) was used as shown in **Figure 1** [16]. The nanoindentation measurement has been described elsewhere [16]. The indentation experiment was performed at an 80- μN load, with both the loading and unloading times being 5.0 s. A diamond tip with an approximately 100-nm radius was used [17].

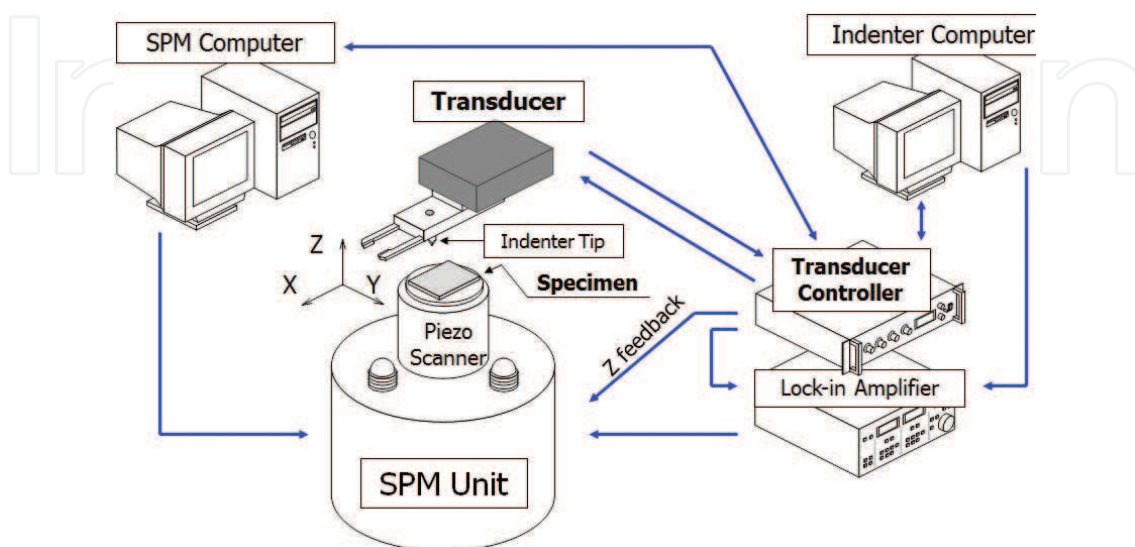


Figure 1. Schematic diagram of the scanning probe microscope and dynamic stiffness measurement system.

2.3. Microwear evaluation

The wear properties of the untreated and CF₄-treated PC samples were evaluated by a microwear test technique using AFM, where a cantilever with a pyramidal diamond tip (radius ~50 nm, Hysitron Inc.) was used. A schematic of the wear test is shown in **Figure 2**, wherein the diamond tip was slid against the sample surface. The wear test was conducted by scanning an area of $1 \times 1 \mu\text{m}^2$ and by applying varying loads of 0.5, 1.0, and 2.0 μN . The observation area was of $3 \times 3 \mu\text{m}^2$ [16].

2.4. Nanoprocessing of lines and dots

Line nanoprocessing was performed on untreated and CF₄-treated PC samples by using a diamond tip with a radius less than 50 nm (SPI 3800N, Seiko Instrument Inc. SII) [16]. The spring constant of the cantilever and tip was 45-51 N/m. An applied load was 150 nN. As shown in **Figure 3** [16], 500-nm-long lines and spaces were produced at 66- and 62-nm intervals on untreated and CF₄-treated PC samples, respectively, in an $800 \times 800 \text{ nm}^2$ scanning area. Second, dots were produced at intervals of 45 and 40 nm on the untreated and CF₄-treated PC samples, respectively, by applying a load of 150 nN.

2.5. Evaluation of viscoelastic properties of processed area

Viscoelastic properties were evaluated using the force modulation method of scanning probe microscopy (SPM) as shown in **Figure 4** [18, 19]. This apparatus was added to a nanoindentation system along with a lock-in amplifier. The Berkovich-type diamond indenter, where

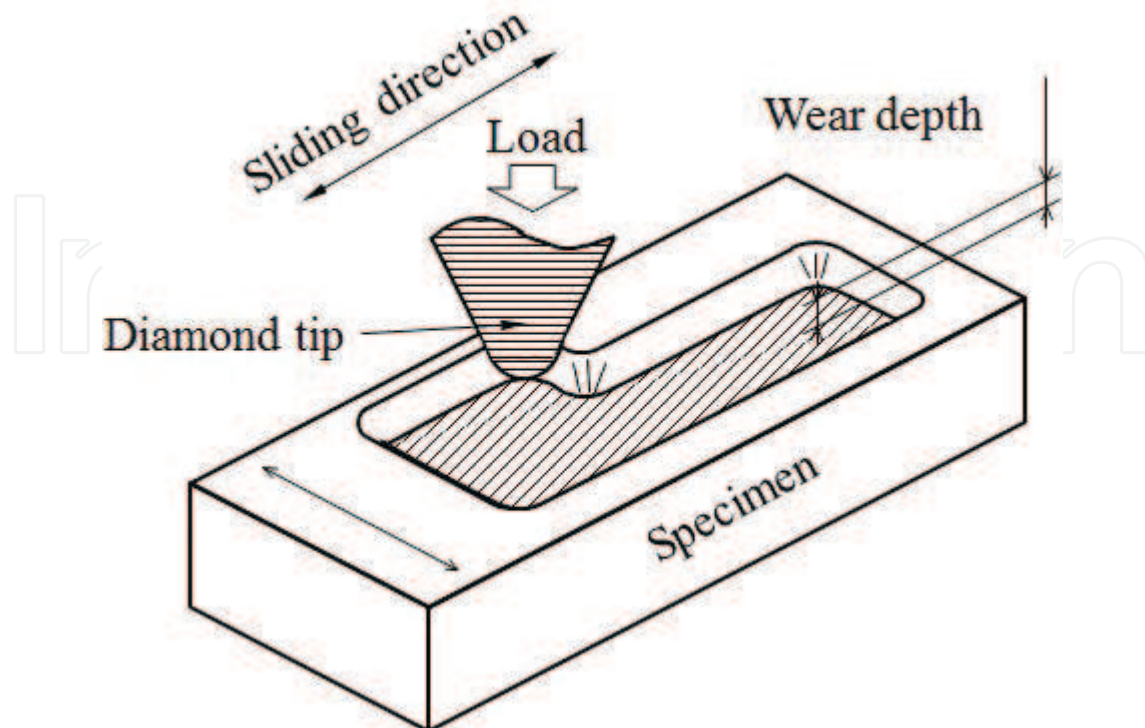


Figure 2. Schematic image of the micro-wear test by atomic force microscopy.

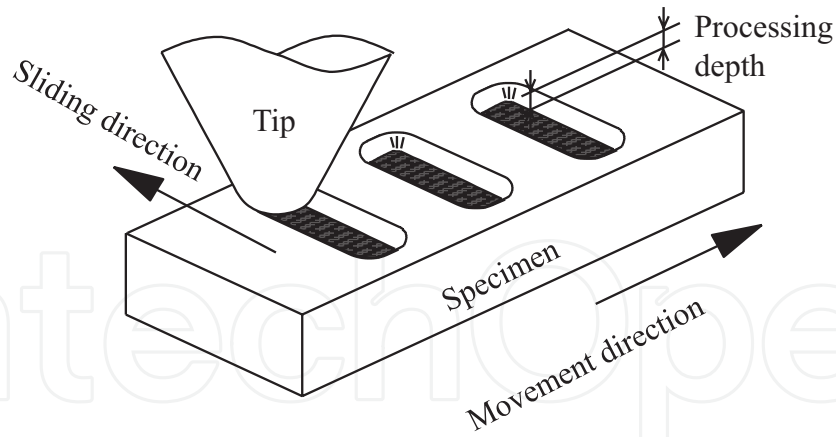


Figure 3. Schematic image of line processing by atomic force microscopy.

a vibration in the vertical direction was applied, was conducted to scan on the sample. As the phase lag and displacement of the tip cantilever were measured via the response of the tip indenter, which possessed a transducer controller, the viscoelastic properties such as the storage modulus, loss modulus, and $\tan\delta$ were obtained from the force modulation [18]. The method in detail was reported in our previous study [16]. With a 100-nm-radius equilateral-triangle pyramidal diamond indenter, these tests were performed under loads varying from 5 to 35 μN , a load amplitude of 5 μN , and a frequency of 400 Hz [16]. After the tests, the sample was scanned using the same tip under a load of 2 nN with a vibration of a frequency of 50 Hz. Viscoelastic properties such as storage modulus, loss modulus, and $\tan\delta$ were evaluated by means of atomic force microscopy [18].

To evaluate the viscoelastic properties, the dynamic model and force modulus of the AFM system were used (**Figure 4**). In this method, the dynamic mechanical properties (e.g., storage and loss moduli) were measured when the scanner was vibrated in the z-axis direction, which was possible when the dynamic response of the indenter of the AFM was well calibrated and modeled. **Figure 5** shows the correlated sinusoidal force and displacement curves, from which the mechanical properties can be calculated using well-established models. The amplitude and phase shift can be used to calculate the contact stiffness using a dynamic model [18], whose standard analytical solution is given below.

The amplitude of the displacement signal (X_0) and the phase shift between the force and displacement (Φ) are given as

$$X_0 = \frac{F_0}{\sqrt{(k - m\omega^2)^2 + [(C_i + C_s)\omega]^2}}, \quad (2)$$

$$\Phi = \tan^{-1} \frac{(C_i + C_s)\omega}{k - m\omega^2} \quad (3)$$

where F_0 is the ac force amplitude, m is the indenter mass, ω is the frequency (rad/s), and C_s and C_i are the damping coefficients of the specimen and the air gap in the capacitive displacement sensor, respectively. The combined stiffness, k , is given by

$$k = K_s + K_i, \quad (4)$$

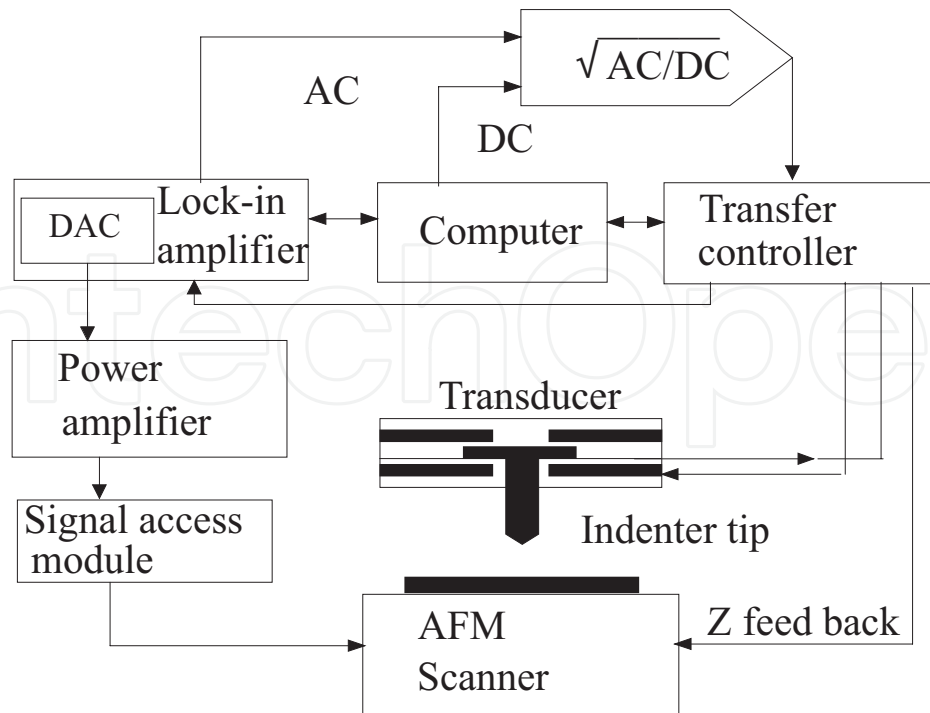


Figure 4. Schematic diagram of the atomic force microscopy system for evaluating the viscoelastic properties.

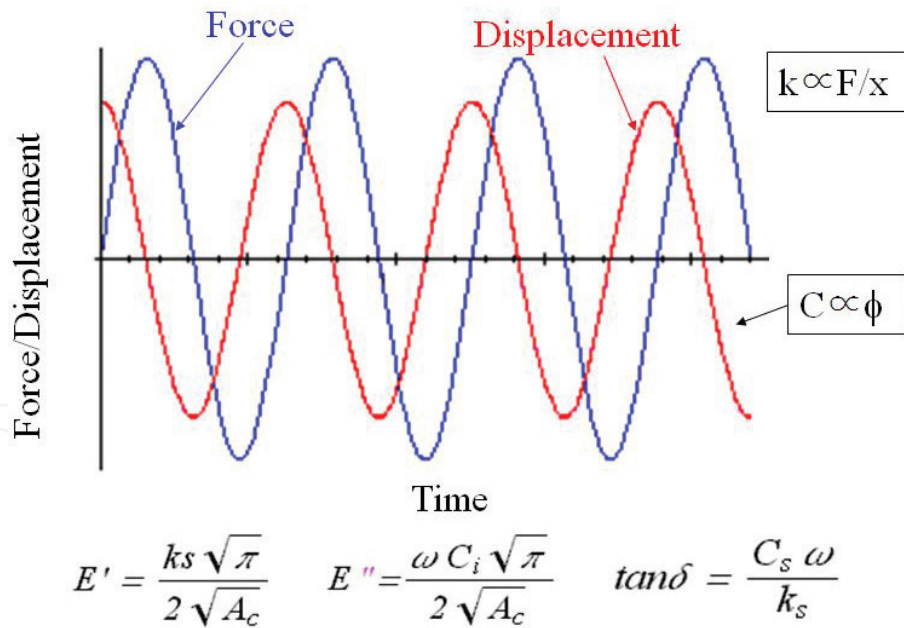


Figure 5. Example of the sinusoidal force/displacement data.

where K_s is the contact stiffness and K_i is the spring constant of the leaf springs holding the indenter shaft. The storage modulus (E'), loss modulus (E''), and $\tan \delta$ can now be found as

$$E' = \frac{k_s \sqrt{\pi}}{2 \sqrt{A_c}} \quad (5)$$

$$E'' = \frac{\omega C_s \sqrt{\pi}}{2 \sqrt{A_c}}, \quad (6)$$

$$\tan \delta = \frac{C_s \omega}{k_s}, \quad (7)$$

where δ is the phase lag between the force and displacement. Eqs. (5)–(7) are used to calculate the storage and loss moduli and to study the viscoelastic properties of polymeric materials [20].

3. Result and discussion

3.1. Measurement of surface-free energy

The effects of the fluorocarbon plasma treatment upon PC samples were evaluated by measuring surface contact angle and surface-free energy. Distilled water, methyl iodide, and n-hexadecane were used in this study. **Figure 6** shows the drop-profile images of the samples, and the measured values of the contact angle and surface-free energy are listed in **Table 1** [16]. **Figure 6** shows that the contact angles of the CF_4 -treated PC are greater than those of the untreated PC, while the measured surface-free energies are 19.2 mN/m for the untreated PC and 16.1 mN/m for the CF_4 -treated PC. These results show that the surface tension of the PC material is reduced after fluorocarbon plasma treatment. It is possible that the C-F compound, which is a peculiarity of polymer materials and has a weak C-F bond interaction, was formed on the PC sample by the fluorocarbon plasma treatment [16, 19, 21, 22].

3.2. Nanoindentation properties

Figure 7 shows the load displacement curves of untreated and CF_4 -treated PC samples obtained in the nanoindentation test with a maximum applied load of 80 μN . The maximum

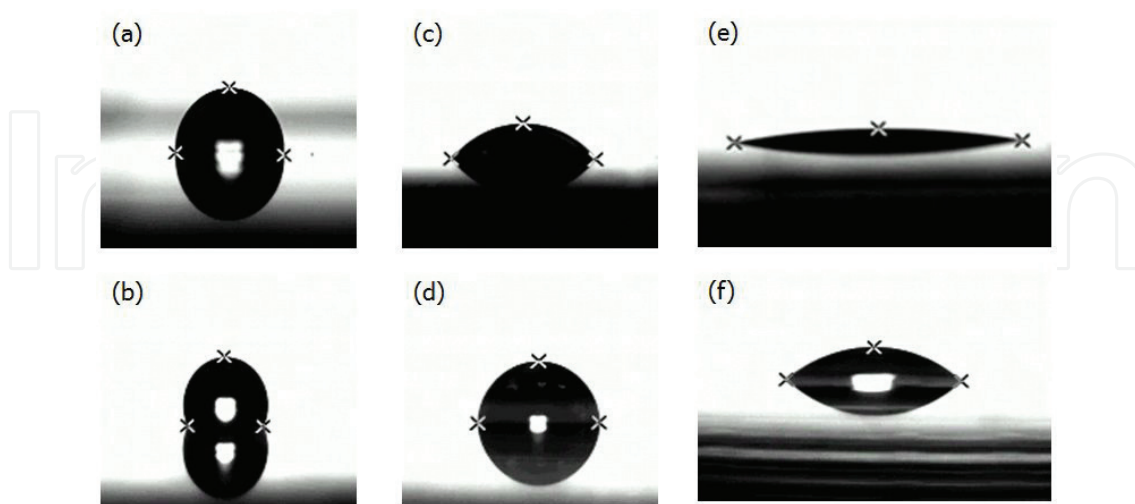


Figure 6. Drop profiles on the untreated and CF_4 -treated PC samples. The profiles show drops of refined water on the (a) untreated and (b) fluorinated samples; drops of methylene on the (c) untreated and (d) fluorinated samples; and drops of n-hexadecane on the (e) untreated and (f) fluorinated samples.

	Contact angle (°)			
	Refined water	Methylene iodide		<i>n</i> -hexadecane
Untreated polycarbonate	95.8	84.2		36.6
CF ₄ -treated polycarbonate	103.5	89.5		44.8
	Surface-free energy (mN/m)			
	Dispersion force (γ^d)	Dipole force (γ^{sp})	Hydrogen bond (γ^{sh})	Surface free energy (γ^s)
Untreated polycarbonate	16.5	0.0	2.7	19.2
CF ₄ -treated polycarbonate	14.8	0.0	1.3	16.1

Table 1. Values of drop-contact angles (upper) and surface-free energies (lower) for untreated (polycarbonate) and CF₄-treated (fluorinated polycarbonate) samples.

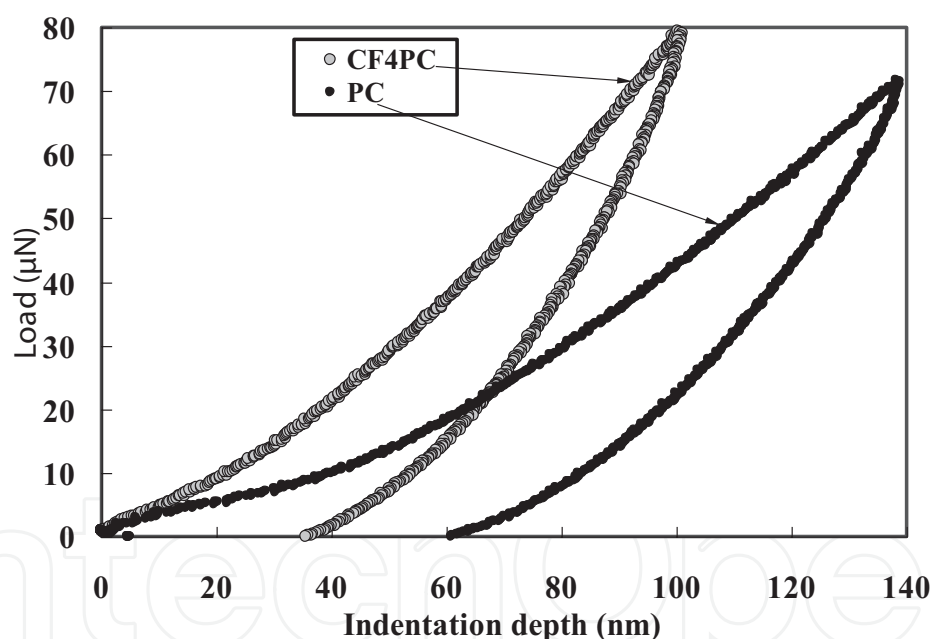


Figure 7. Load versus indentation depth (displacement) for (a) untreated (PC) and (b) CF₄-treated (CF₄-PC) PC samples at a peak load of 80 μ N.

indentation depths are approximately 132 nm for the untreated PC and approximately 100 nm for the CF₄-treated PC [16]. It can be clearly seen that the residual depth (deformation) of the CF₄-treated PC is smaller than that of the untreated PC, indicating that more plastic deformation occurs on the untreated PC. Meanwhile, it is believed that the hardness of the PC sample is improved by the fluorocarbon plasma treatment [16].

3.3. Wear properties of untreated and CF₄-treated PC

Wear tests were performed by sliding a tip repeatedly over the same sample area under applied loads ranging from 0.5 to 35 μN . A sinusoidal signal with a frequency of 400 Hz was added to the tip. **Figures 8 and 9** show the profile AFM images of wear marks made at loads 0.5, 1, and 2 μN [16]. The square wear marks in the CF₄-treated PC are clearly formed compared with those in the untreated PC, whereas the wear depths of the former are smaller than those of the latter. Wear marks with a depth ranging from 2 to 13 nm were formed on the CF₄-treated PC, indicating that it is possible to perform nanoprocessing on it.

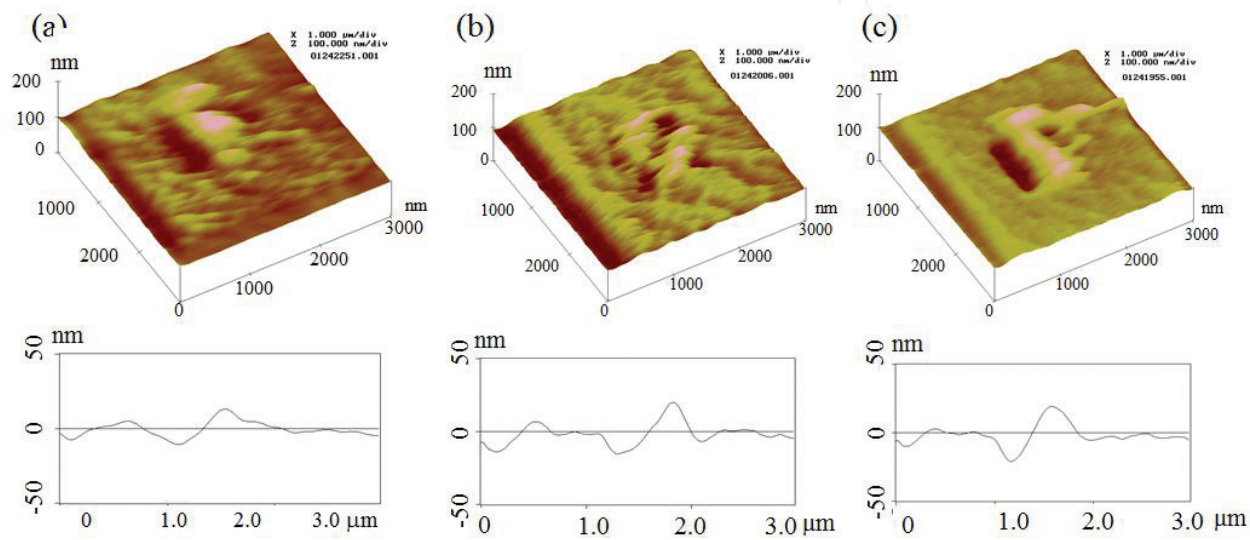


Figure 8. Atomic force microscope images (upper) and line-scan profiles (lower) of wear marks on untreated PC, created at loads of (a) 0.5, (b) 1, and (c) 2 μN .

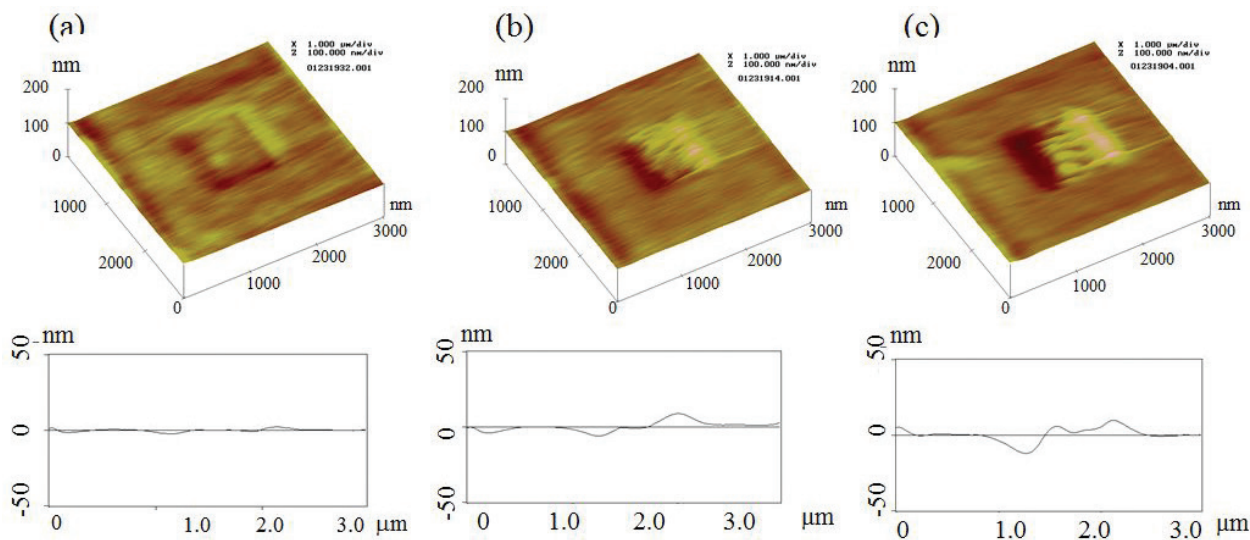


Figure 9. Atomic force microscope images (upper) and line-scan profiles (lower) of wear marks on CF₄-treated PC, created at loads of (a) 0.5, (b) 1, and (c) 2 μN .

Figure 10 shows a plot of wear depth versus load for the untreated and CF_4 -treated PC. The wear tests were repeated five times and exhibited a high degree of repeatability with almost no changes in the observed trend [16]. It is found that the wear resistance of the PC sample is improved with fluorocarbon plasma treatment.

3.4. Load dependence of nanoprocessing properties

To clarify the nanometer-scale processing properties of the PC samples, these were investigated using load as a factor. **Figure 11** shows the horizontal waveform and magnitude of the friction force on the tip for varying loads. The friction force is measured by sliding the tip on the sample for one trace and a reciprocal retrace, where the tip is varyingly loaded with 0, 130, 190, or 250 nN. The untreated PC (**Figure 11a**) shows large and unstable friction forces, whereas the CF_4 -treated PC (**Figure 11b**) shows small and stable friction forces at the same processing loads. **Figure 11c** shows the dependence of the magnitude of the friction force upon load for the untreated and CF_4 -treated PC samples, where it is clear that the friction force of the CF_4 -treated PC is smaller than that of the untreated PC.

Figure 12 shows the shape and depth images of grooves (traces) processed on the untreated (**Figure 12a**) and CF_4 -treated (**Figure 12b**) PC samples. As shown in **Figure 12a**, the groove shapes in the untreated PC are not clearly visible, and lumps and processing residues are generated along the processing grooves, which indicate that the processed grooves generate deformations. By contrast, the grooves are clearly formed in the processed area of the CF_4 -treated PC, as shown in **Figure 12b**.

Figure 12c shows the mean heights and depths of the deformation components (lumps and grooves) at the center of the processed grooves of the untreated PC for varying loads. The lump height (deformation height) increases with processing tip loads from 50 to 250 nN. However, with loads exceeding 300 nN, the mean height of the processed grooves decreases to negative values, which indicates that the grooves are formed by material removal. These

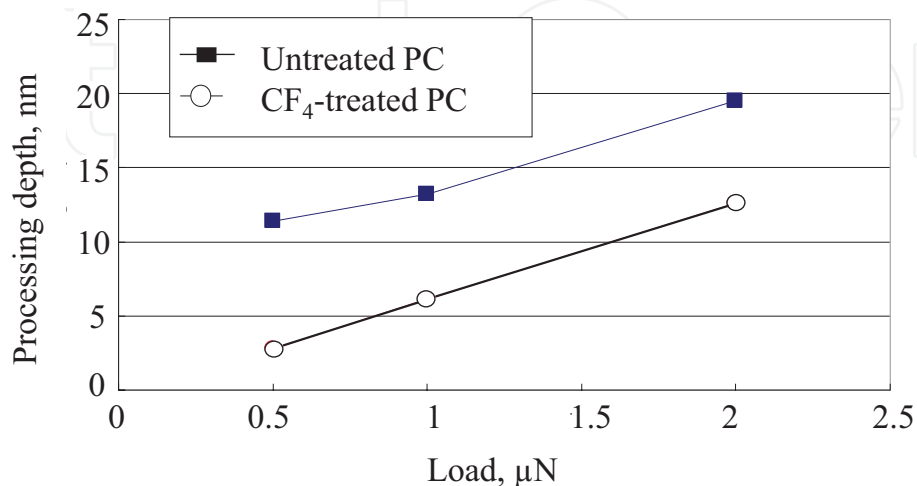


Figure 10. Wear depth as a function of load for untreated (filled squares) and CF_4 -treated (empty circles) PC samples.

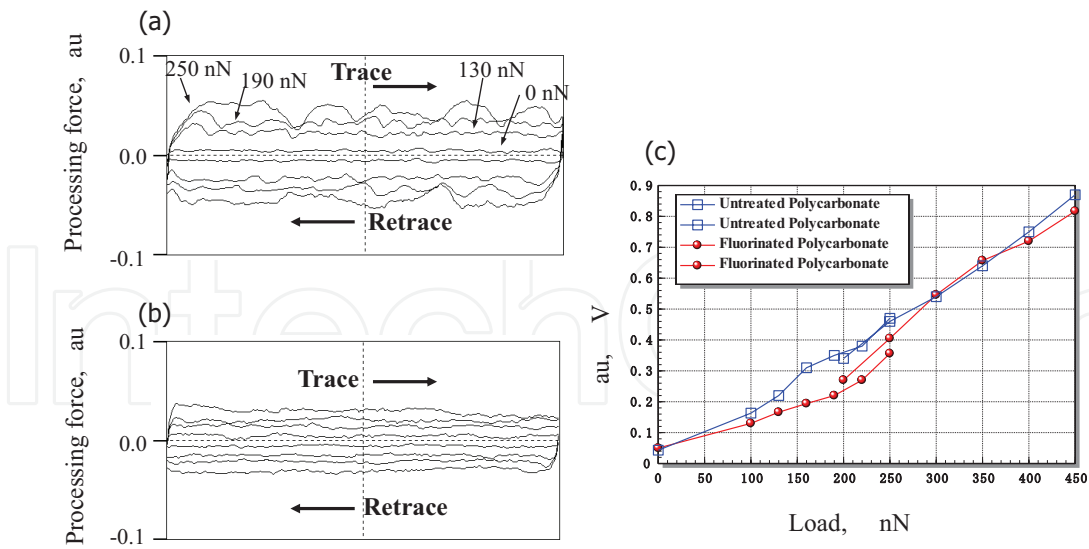


Figure 11. Friction force measured at varying loads for the (a) untreated and (b) CF₄-treated PC samples, with the friction force waveforms arbitrarily scaled from the zero axis (dashed line) in the order of 0, 130, 190, and 250 nN for both the trace and retrace plots. (c) Magnitude of the friction force as a function of tip load for both samples.

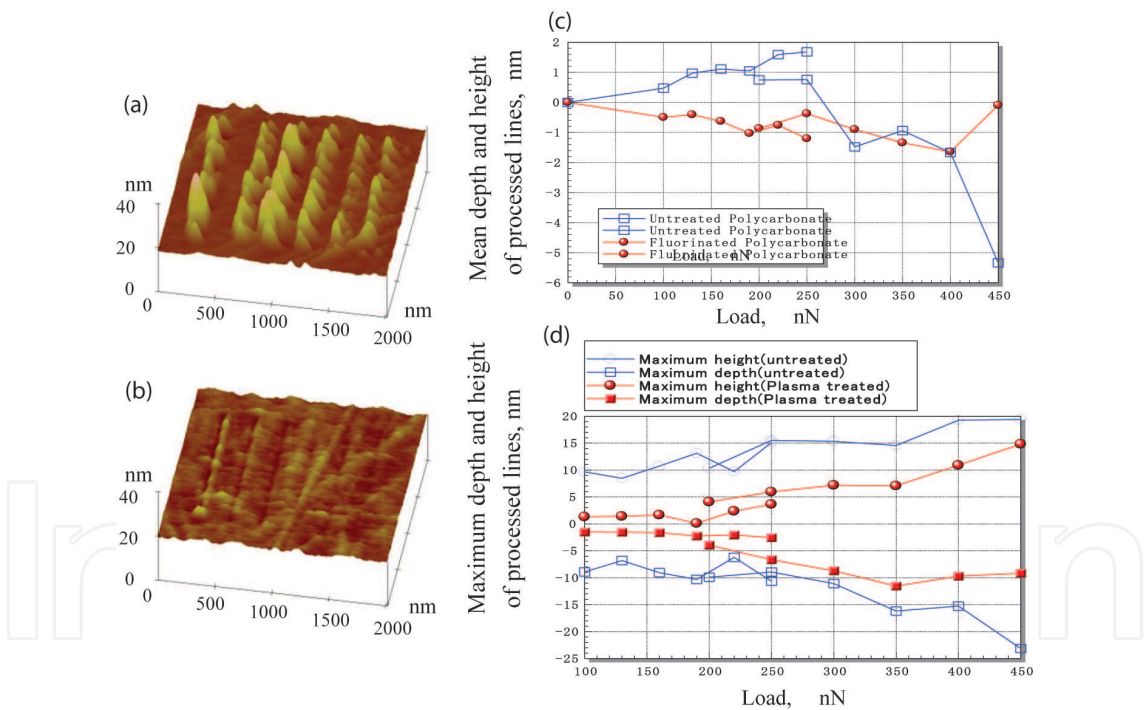


Figure 12. Atomic force microscope images of grooves processed on the (a) untreated and (b) CF₄-treated PC samples. Depths of processed grooves for the samples, plotting the (c) mean depth and the (d) maximum and minimum depths of the groove centers.

results illustrate that molecular chains are dragged and deformed at loads less than 300 nN, while at loads greater than 300 nN there is removal of the PC. It is concluded that the molecular chains of the PC material are dragged by the friction force between the tip and processed surface at low loads, which results in expanded distances between the molecules.

As a result, lumps are formed. As the load increases further, the friction force increases to a level sufficient to remove part of the molecular chain, thereby forming a groove. By contrast, as shown in **Figure 12d**, the CF_4 -treated PC exhibits very different results from that of the untreated PC. Removal processing in the treated sample begins from 100 nN loads, and the major restructuring of the processed surface is not observed. It is concluded that the friction force of the CF_4 -treated PC is reduced by the fluorination treatment and that the molecular chain dragging that causes the lumps and surface roughening is suppressed.

3.5. Nanometer-scale dot and line processing

Dots with intervals of 45 nm were processed by sliding the tip over the untreated PC surface (**Figure 13a**), creating dots whose shapes are not uniform. Dots with inter-dot intervals of 40, 35, and 30 nm were also processed on the CF_4 -treated PC and are, respectively, shown in **Figure 13b–d**, where uniformly shaped dots are clearly observed. The line profiles of these fine dots obtained from **Figure 13** AFM images are given in **Figure 14**, which clearly indicate that fine-dot processing is realized on the CF_4 -treated PC sample. Because fine processing performed in a region of $25 \times 25 \mu\text{m}^2$ is thought necessary for the realization of 1 Tbit/inch² recording, these results demonstrate that this level of processing can be realized using a sharp tip.

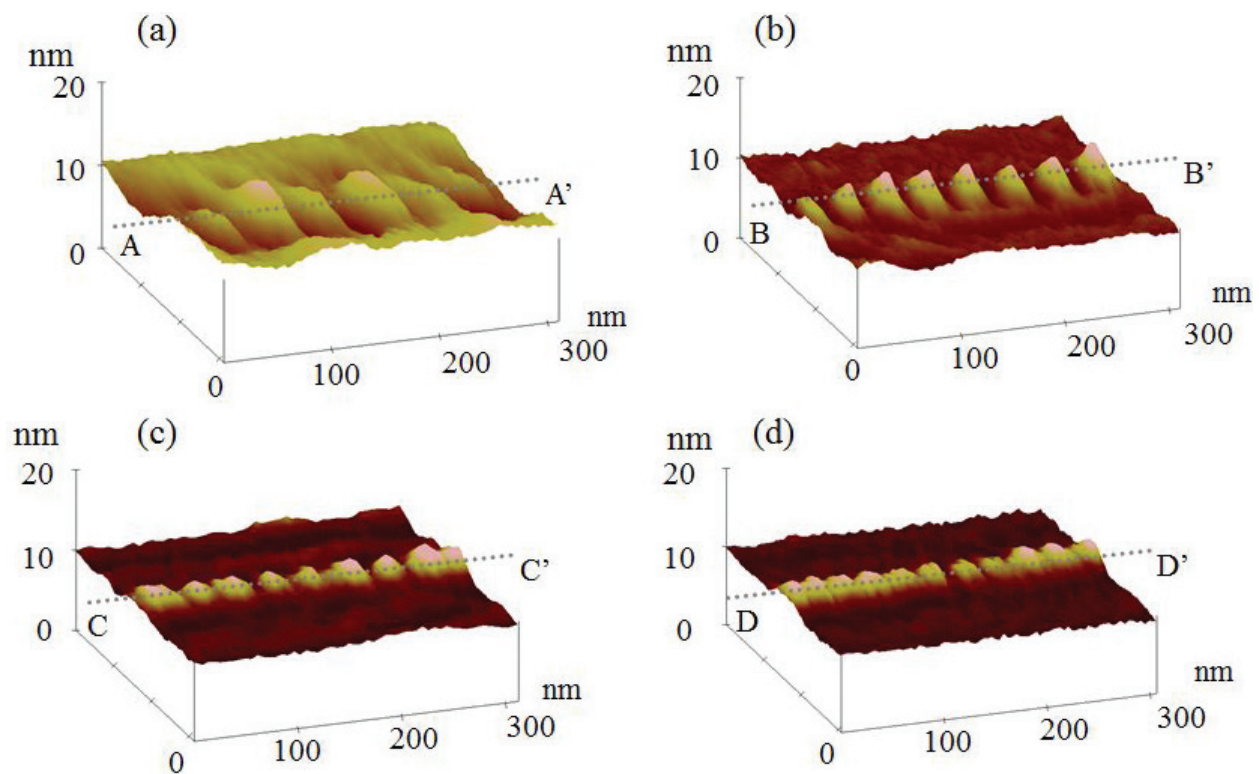


Figure 13. Atomic force microscope images of the fine dots processed with varying dot intervals on untreated and CF_4 -treated PC samples. Shown are images of dots processed on (a) untreated PC (groove interval 45 nm), and CF_4 -treated PC with groove intervals of (b) 40, (c) 35, and (d) 30 nm. The lines (A–A'), (B–B'), (C–C'), and (D–D') mark the line from which sectional profiles are obtained for **Figure 14**.

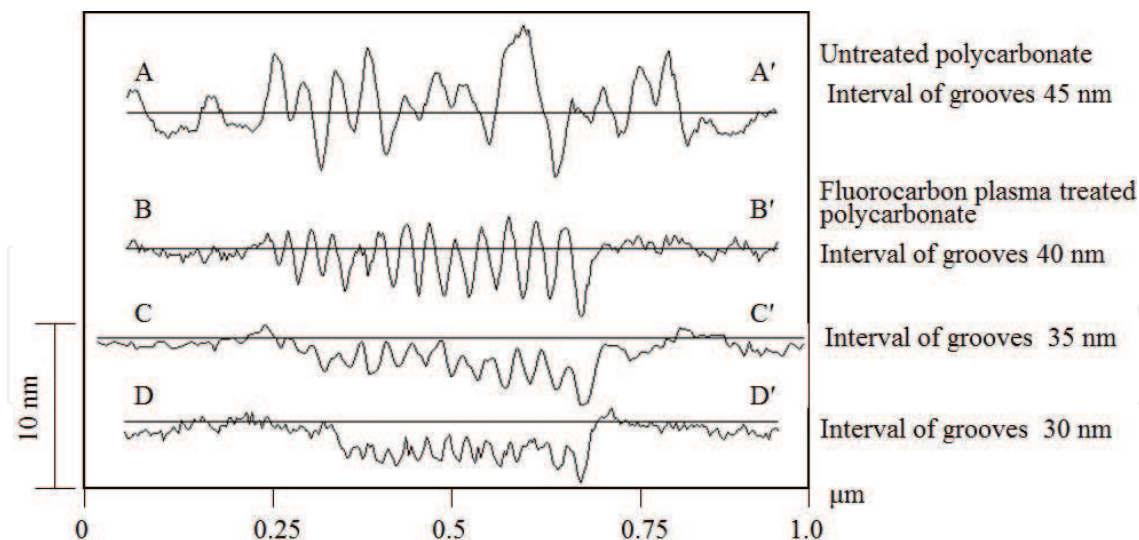


Figure 14. Atomic force microscope sectional profiles of fine dots processed at varying dot intervals on untreated and CF_4 -treated PC samples. Plotted are profiles of dots processed on untreated PC (groove interval 45 nm) (A–A'), and CF_4 -treated PC with groove intervals of 40 (B–B'), 35 (C–C'), and 30 (D–D') nm.

Lines were processed on untreated PC by scanning a DLC-coated tip under a load of 150 nN at a 66-nm line interval. As shown in the AMF images and line profiles in **Figure 15a**, no obvious formation of precise lines are seen, but many lumps with heights approximately 3–5 nm are generated. As discussed earlier, these lumps are formed when the molecule chains of the polymer PC surface are dug up by tip scanning, causing plastic deformations in the processed area. It is clear that precise fabrication of fine lines is impossible on the untreated PC. **Figure 15b** shows AFM images and line profiles of the fine lines processed on the CF_4 -treated PC by scanning a DLC-coated tip under a load of 150 nN at a 62-nm line interval [16]. Macroscopically, precision processing is realized. Contrasted with the roughness of the unprocessed area, the shapes of the formed lines are uniform and a change in depth can be observed. Furthermore, it is found that the roughness of the surface does not vary with the processing. This is possibly because that the processing resistance becomes constant, and any variation is virtually negligible during processing [16]. The processing properties of the CF_4 -treated PC can be possibly improved because of a decrease in the PC friction coefficient of the PC with fluorocarbon plasma treatment.

Regarding the nanometer-scale processing characteristics of the CF_4 -treated PC, because the surface-free energy is reduced with CF_4 treatment, it is possible that fine dots are produced while scanning the tip at low loads. However, the processing is typically performed more than 10 times, and we therefore evaluated repetitive processing, as shown in **Figure 16**. On the untreated PC, shown in **Figure 16a**, there are quite large and irregular lumps generated at the peripheral areas of the scanned regions, which is thought to be because molecule chains are easily dug up on this sample even at low loading forces. Therefore, it is difficult to perform high-precision line processing at the nanometer scale on the untreated PC. For the CF_4 -treated PC shown in **Figure 16b**, the interaction between atomic particles is weak owing to the C-F compound, and this produces a low frictional force during tip scanning that is insufficient to dig up the molecule chains. Therefore, fine processing at the nanometer scale can be successfully realized at low loads.

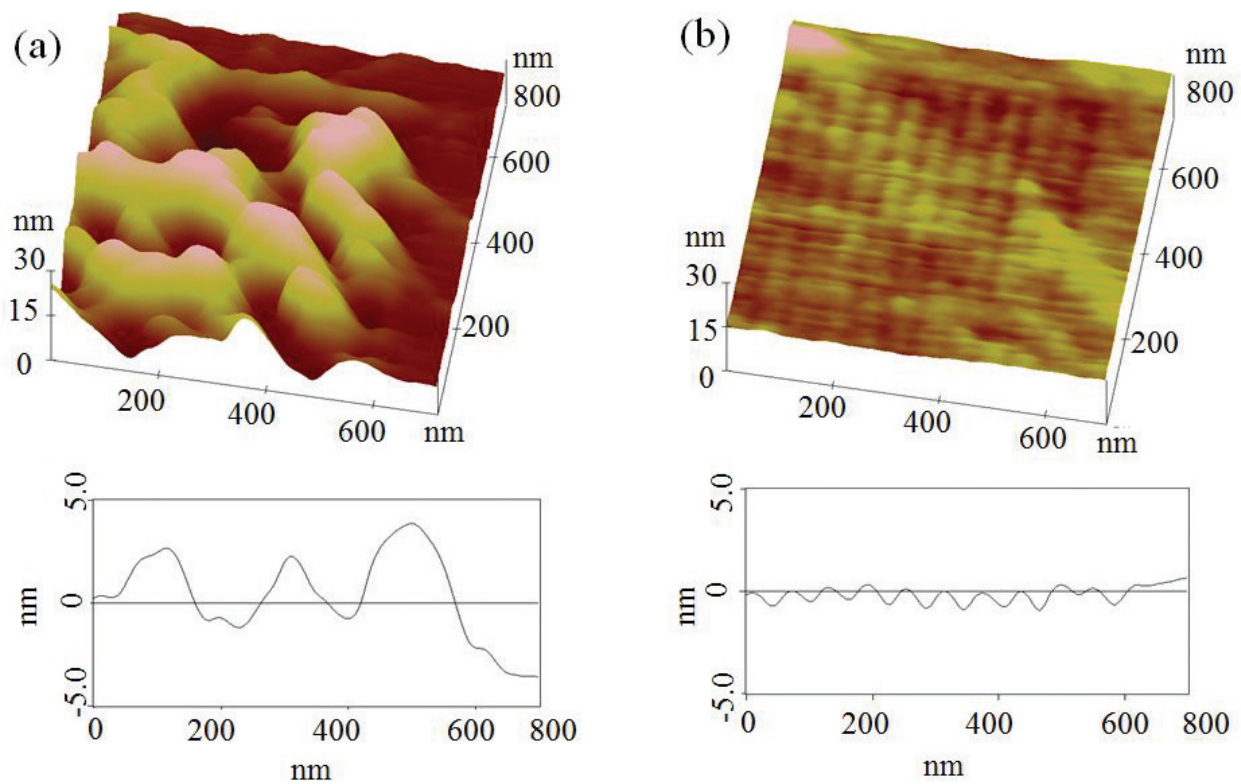


Figure 15. Atomic force microscope images (upper) and line-scan profiles (lower) of the lines and spaces processed at a load of 150 nN on (a) untreated PC with a 66-nm interval and (b) CF₄-treated PC with a 62-nm interval.

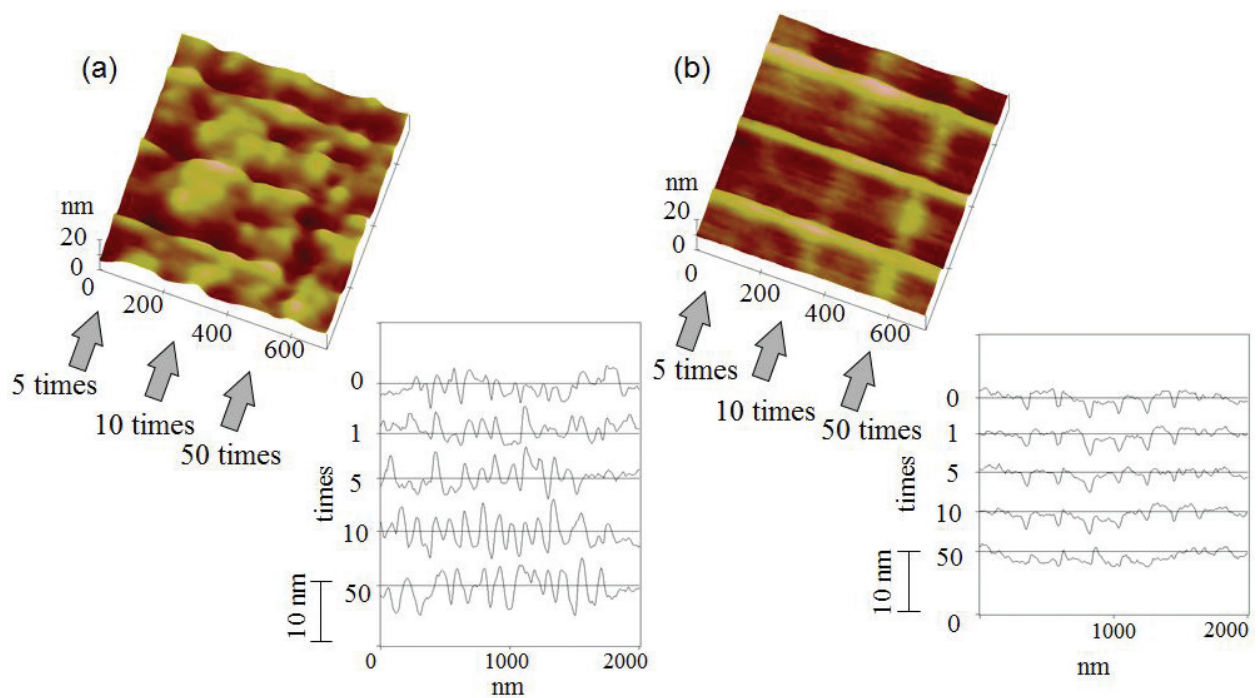


Figure 16. Atomic force microscope images (upper) and line-scan profiles (lower) of regions repetitively scanned 1, 5, 10, and 50 times on the (a) untreated and (b) CF₄-treated PC samples.

3.6. Evaluation of viscoelastic properties

To investigate the effect of the fluorocarbon plasma upon precision processing, the viscoelastic properties were evaluated by a wear test on the untreated and CF_4 -treated PC. **Figure 17** plots the storage (**Figure 17a**) and loss (**Figure 17b**) moduli of the worn (processed) and unworn (unprocessed) areas of the CF_4 -treated PC and of the unprocessed and untreated PC. It can be seen in the plot that the storage modulus of the unprocessed CF_4 -treated PC (i.e., CF_4 -treated PC without wear) is lower than that of the untreated PC and the processed CF_4 -treated PC (i.e., CF_4 -treated PC with wear). It is also observed that the unprocessed CF_4 -treated PC exhibits significantly smaller values of the loss modulus (as well as lower stiffness and damping values, c.f. **Figure 18**) compared with those of the untreated PC and the processed CF_4 -treated PC. As shown in **Figure 17**, at loads ranging from 5 to 10 μN on the CF_4 -treated PC, the value of the storage modulus is very small, while the loss modulus is almost at zero at a load of $\sim 8 \mu\text{N}$. Owing to the adhesion that exists between a tip and a surface, the interaction between the tip and the surface of the CF_4 -treated PC sample is smaller than that of the untreated PC and processed CF_4 -treated PC samples. When analyzing the CF_4 -treated PC, it may be speculated that the energy loss of its interface is extremely small at low loads because the surface-free energy is low in the C-F compound structure and the interaction between a tip and sample surface is small when the tip is scanning the sample surface.

However, as the load increases, both E' (storage modulus) and E'' (loss modulus) show an increasing trend, with the untreated PC and processed CF_4 -treated PC increasing in a similar fashion. This similar tendency is shown in both the untreated PC, whose atomic interactions are strong, and the CF_4 -treated PC, whose atomic interactions are weak, and the tendency is mainly affected by the adhesion between a tip and processing surface under a low load. It is observed in these samples that when the interaction between the tip and the sample surface is raised along with the gradually increasing load, the stiffness and damping are also seen to increase (**Figure 18**).

From **Figures 17b** and **18a**, the loss modulus and stiffness of the unprocessed CF_4 -treated PC sample are significantly lower than those of the untreated PC and processed CF_4 -treated PC

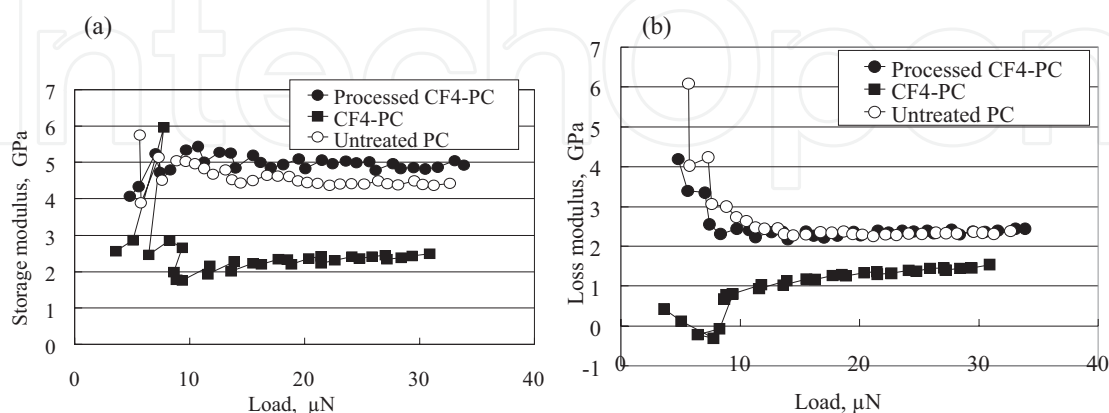


Figure 17. Plots of the viscoelastic properties at loads ranging from 5 to 35 μN , showing the (a) storage and (b) loss moduli of untreated PC (empty circles) and CF_4 -treated PC (filled-squares) samples with no wear induced on their surfaces, and a processed CF_4 -treated PC (filled-circle) sample, where “processed” indicates that wear is induced on its surface.

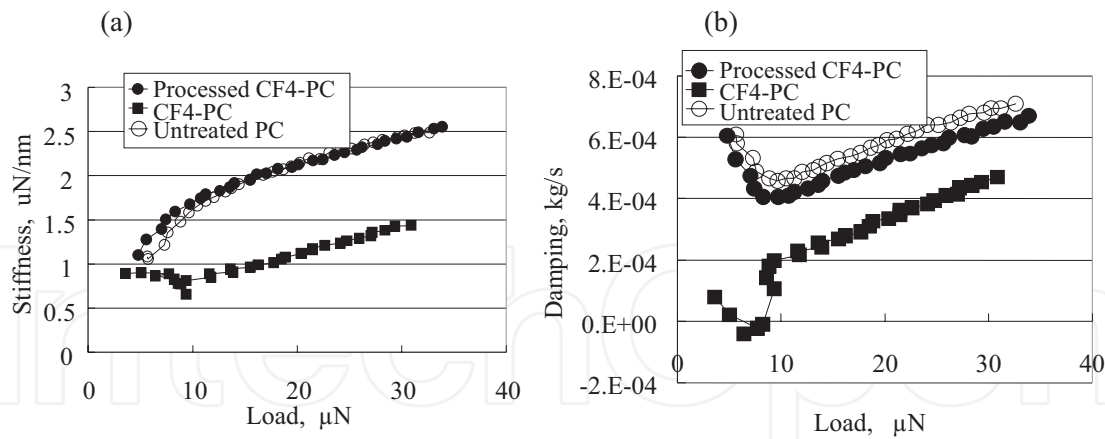


Figure 18. Plots of the viscoelastic properties at loads from 5 to 35 μN , showing the (a) stiffness and (b) damping of untreated PC (empty-circle) and CF₄-treated PC (filled-square) samples with no wear induced on their surfaces, and a processed CF₄-treated PC (filled-circle) sample, where “processed” indicates that wear is induced on its surface.

samples [16]. Compared with the untreated and processed CF₄-treated PC samples, since the unprocessed CF₄-treated PC has a fluorocarbon plasma layer on its surface, the interaction between the tip and its surface is weak during processing. As a result, the unprocessed CF₄-treated PC shows a lower loss modulus and stiffness [16, 19]. It is thought that C-F compound might be formed on the PC during the fluorocarbon plasma treatment, which results in a reduction of the shear resistance of the treated surface. **Figure 18b** shows that the damping of the CF₄-treated PC decreases owing to C-F bonds.

As shown in **Figure 19**, at a load ranging from 0 to 8 μN , the $\tan\delta$ -value of the unprocessed CF₄-treated PC sample was much lower than those of the untreated PC and processed CF₄-treated PC samples. It was known that $\tan\delta$ is the ratio of loss to the storage and is called damping [23]. The results showed that the unprocessed CF₄-treated PC sample has a small $\tan\delta$ -value (damping value) at less than 10- μN load because the CF₄-plasma treatment layer on its surface still remained, so that the interaction between the tip and its surface is small

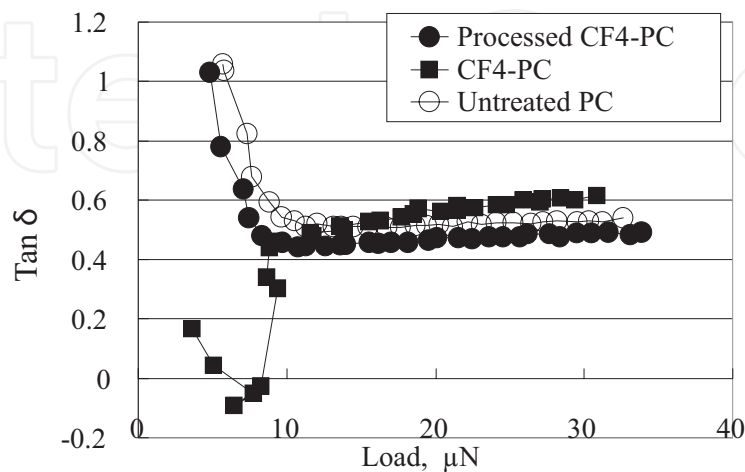


Figure 19. Plot of a viscoelastic property at loads ranging from 5 to 35 μN , showing the $\tan\delta$ of untreated PC (empty circles) and CF₄-treated PC (filled-square) samples with no wear induced on their surfaces, and a processed CF₄-treated PC (filled-circle) sample, where “processed” indicates that wear is induced on its surface.

owing to the formed C-F bonds [16, 19]. However, the $\tan\delta$ -value of the unprocessed CF_4 -treated PC sample sharply increased to be close to those of the untreated and processed CF_4 -treated PC samples at the load of 10 μN and it became even slightly higher than others when the load was more than 10 μN , indicating that the CF_4 -plasma treatment layer on the unprocessed CF_4 -treated PC sample was removed by tip scanning at the 10 μN and more load, resulting in the interaction being increased [16, 19].

4. Conclusion

Based on the surface modification and nanometer-scale mechanical processing of PC and the evaluation of its viscoelastic properties using AFM, it is feasible to realize high-density storage memory using modified PC as a media.

Our current study focuses upon the evaluation of various viscoelastic properties of untreated PC, processed CF_4 -treated PC (i.e., wear induced on its surface), and unprocessed CF_4 -treated PC (i.e., no wear induced on its surface), whereby the following points can be concluded:

1. A PC material was modified by fluorocarbon plasma treatment, whereby the surface-free energy of the PC was reduced. Nanometer-scale line and dot processing were realized owing to a subsequent reduction in the interaction force between the tip and the fluorinated sample.
2. The indentation evaluation result shows that the plastic deformation of the PC was improved by the fluorocarbon plasma treatment. The realization of nanometer-scale line and dot processing is possible because the plastic deformation caused the surface damage and wear when attempting fine processing at low loads was reduced. Furthermore, the CF_4 -PC shows its super wear-resistant properties to prevent the development of deformations.
3. The viscoelastic properties of the CF_4 -PC show the values of loss modulus, stiffness and $\tan\delta$ lower than those of the untreated PC, which indicates that the shear resistance of PC was reduced. It is possible that the C-F combination was formed on the PC by the fluorocarbon plasma treatment, which would imply that the processing resistance decrease was owing to the weak interaction of the C-F bonds.
4. The storage and loss moduli, stiffness and damping of a processed area on the CF_4 -treated PC were practically the same as those of untreated PC because the CF_4 -treated layer of the processed area was removed by tip scanning. Therefore, the processed areas exhibited the same viscoelastic properties as the untreated PC.

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