

# Electric Surface Modification of Diamond Like Carbon Film

Member Shigeki Tsuchitani (Wakayama University)  
 Non-member Yoshinori Nakano (Wakayama University)  
 Non-member Yoshihiro Imagawa (Wakayama University)  
 Non-member Shigeru Hirono (Advanced Film Technology Inc.)  
 Non-member Reizo Kaneko (Wakayama University)

Local surface modifications of a diamond like carbon (DLC) film are carried out by applying voltages to conductive (Au coated) AFM probes in the contact mode. The DLC is deposited on a silicon substrate by ECR sputtering. When DC voltages are applied as the probe is scanned, two types of modifications such as hollows and mounds are formed in negative bias (-3 ~ -5V). When negative voltage pulses (-15V) are applied to the probe contacting with a point on the DLC, small pits are formed. Diameters of the pits decreases with decrease of the pulse width in the range from 1000ms to 10ms. The pit formed by the voltage pulse with 10ms width has 20nm diameter.

**keywords:** point recording, surface modification, diamond like carbon, atomic force microscope

## 1. Introduction

One of potential applications of scanning probe microscope (SPM)-based techniques is high density data storage. As the tip of an SPM probe is very sharp, we can record and read small dots or letters on solid surfaces[1-7]. This technology is called "point recording". A basic technology of the point recording is to form very small patterns having different physical properties from those of the surrounding area, i.e. local surface modifications.

In this paper, we describe the electric surface modifications of a diamond like carbon (DLC) film, especially surface topography changes of the DLC film by applying voltages between a probe of an atomic force microscope (AFM) and the DLC film.

The DLC films are commercially used as protective overcoats of recording media and recording head sliders of magnetic data storage devices or they were applied to sliding parts of electrostatic micromotors[8], since the DLC films are highly wear-resistant materials. Therefore, if the surface modifications of the DLC films are possible by using the SPM probes, they are very suitable recording materials for high density recording devices using the point recording technique, because they have excellent mechanical properties.

## 2. Experimental method

The DLC film was deposited on a silicon substrate by the electron cyclotron resonance plasma (ECR) sputtering method. The wear resistances of the DLC films formed by this method are almost same as that of bulk diamond and are higher than the wear resistances of films deposited by RF sputtering method[9]. The thickness of the DLC film was 25nm. Figure 1 shows an experimental system to modify electrically the surface of the DLC film. Conductive AFM probes of pyramidal shapes coated by Au film were used. The tip radius of the probes was less than 20nm. A resistor R (33.3kΩ) was connected to the sample in a series to evaluate the electric current flowing through the probe.

Modifications were carried out in air by two methods. In the first method, the DC modification voltages  $V=V_{mod}$  were applied to the conductive AFM probe as it was scanned in the contact mode (contacting load: 5nN) on a square area (200nm x 200nm or 800nm x 800nm) of the DLC surface. Scan rate and number of scan lines were 1s/line and 64lines, respectively. The modification voltages were between +5V and -5V. In the second method, the AFM probe was contacted to a fixed position on the surface of the DLC and pulse like modification voltages of -15V with various pulse widths were applied to the AFM probe. Before and after the modification voltages were applied, the topographies of the DLC surface in larger areas including the voltage applied areas or points were observed by the AFM with the probe used in the modifications.

## 3. Results and discussion

At first, we describe the results of the electric modifications by the first method, i.e. the modifications in which the DC

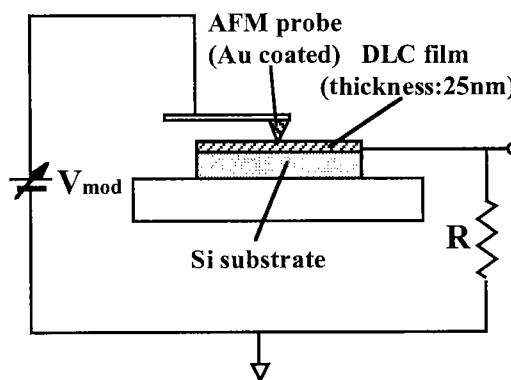
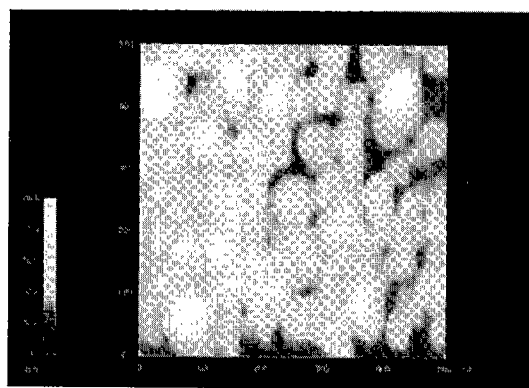
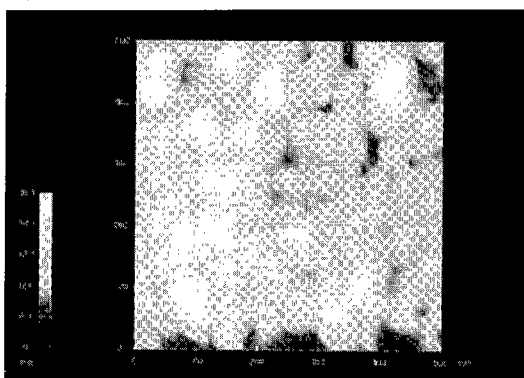


Fig. 1. Experimental system to modify electrically the DLC surface.



(a) Before voltage application

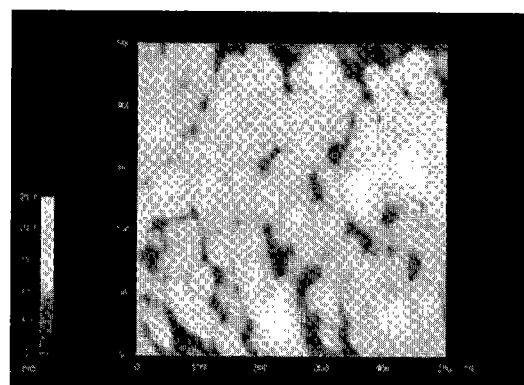


(b) After voltage application

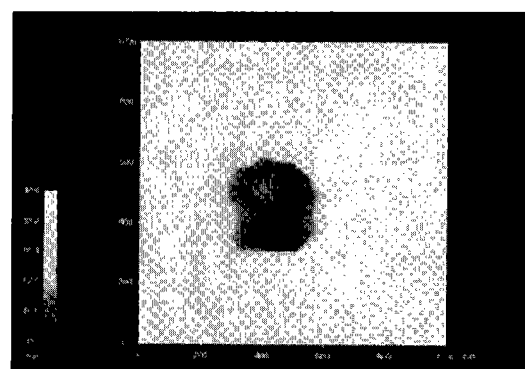
Fig. 2. Topography of DLC film before and after application of +3V to 200nm x 200nm area.

voltages were applied as the probe was scanned. When the modification voltages were positive, changes in the surface topography did not observed except  $V_{\text{mod}} = +3\text{V}$ . Figure 2 shows AFM images of topography before and after the application of the modification voltage +3V. In the images, the areas expressed more brightly have higher surface levels. After the voltage application, some clusters of the DLC in the central part of the image were eliminated.

In the negative modification voltages above -2V, apparent surface changes were not observed. However, when the voltages below -3V were applied, remarkable changes in the surface topography occurred. Shapes of the modified portions depended on the modification voltages. In the voltages  $V_{\text{mod}} = -3\text{V}$  and -4V, only hollows were formed in the area where the modification voltages were applied. Yields with which the hollows were formed were about 10% in the case of  $V_{\text{mod}} = -3\text{V}$  and about 40% in the case of  $V_{\text{mod}} = -4\text{V}$ . Figure 3 is AFM images to show the change in the surface topography by the application of the modification voltage -3V. The hollow of almost square was formed in the voltage applied area. When the modification voltage was -5V, both the hollow and mounds were formed. Figure 4 shows the topographic image of one of microstructures formed by applying  $V_{\text{mod}} = -5\text{V}$ . Around the hollow, some



(a) Before voltage application



(b) After voltage application

Fig. 3. Topography of DLC film before and after application of -3V to 200nm x 200nm area.

radialized mounds were formed. In the modification voltage of -5V, the topography changes occurred in all cases of the voltage applications. In the negative voltage below -2V, the probability that the surface topography changes arose increased with increase of the magnitude of the modification voltage.

Concerning the electric current flowing through the probe during the application of the modification voltage, there was a tendency that the currents when the surface topography changed were much smaller than those (order of  $10\mu\text{A}$ ) when the topographic changes were not observed. This means that a reaction which accompanied decrease in the current took place when the hollows or the mounds were formed on the DLC surface or the surface resistivity of the DLC increased as a result of the modification.

Since the topography changes occurred by the applications of the negative modification voltages in the first method, we tried to form micro pits on the DLC surface by applying negative voltage pulses. Figures 5 and 6 show the topographic images of the micro pits formed by applying single voltage pulses of -15V with different widths. When the pulse widths were 50ms (Fig. 5) and 10ms (Fig. 6), diameters of the pits were about 25nm and 20nm, respectively. The diameter decreased almost linearly with decrease of the pulse width in the range from 1000ms to 10ms.

Electric surface modifications of graphite using SPM were carried out by some researchers[1,10-12]. Graphite is conductive and composed of carbon atoms as well as the present DLC sample. Hosaka et al.[12] reported that two types of surface modifications, such as pits and mounds were observed on the graphite surface by applications of voltage pulses (-5V).

Concerning the polarity of the modification voltage, formations of the distinct hollows and pits were possible in the negative bias of the probe, in our experiment. This polarity agrees with the results in the experiments using graphite by Rabe et al.[10] and Hosaka et al.[12] but is opposite to the polarity as reported by Mizutani et al.[11] also in the experiment using graphite.

The mechanism of the surface modifications of the DLC is now being studied. One possible mechanism by which the hollows and the pits were formed is a chemical reaction between carbon atoms and water molecules, by the analogy of the surface modifications of graphite[11].

#### 4. Conclusions

Local surface modifications of a DLC film deposited on a silicon substrate by ECR sputtering were carried out by applying various bias voltages to an Au coated AFM probe in the contact mode. When DC voltages were applied as the probe was scanned on a square area of the DLC surface, two types of modifications, such as hollows and mounds around the hollows, were formed in negative bias (-3 ~ -5V) of the probe with respect to the DLC. When negative single voltage pulses (-15V) were applied to the probe contacting with the DLC surface, small pits were formed. The diameter of the pit decreased with decrease of the pulse width in the range from 1000ms to 10ms. The pit formed by the voltage pulse with 10ms width had about 20nm diameter.

(Manuscript received June 16, 2000, revised September 25, 2000)

#### References

- [1] T.R. Albrecht, M.M. Dovek, M.D. Kirk, C.A. Lang, C.F. Quate, and D.P.E. Smith: Nanometer-scale hole formation on graphite using a scanning tunneling microscope, *Appl. Phys. Lett.*, 55, 17, pp.1727-1729 (1989)
- [2] R. Kaneko and E. Hamada: Local modification of organic dye materials by dielectric breakdown, *J. Vac. Sci. Technol.*, A8, 1, pp.577-580 (1990)
- [3] H.J. Mamin, P.H. Guethner, and D. Ruger: Atomic emission from a gold scanning-tunneling-microscope tip, *Phys. Rev. Lett.*, 65, 19, pp.2418-2421 (1990)
- [4] R.C. Barrett and C.F. Quate: Charge storage in a nitride-oxide-silicon medium by scanning capacitance microscopy, 70, 5, pp.2725-2733 (1991)
- [5] H.J. Mamin and D. Ruger: Thermomechanical writing with an atomic force microscope tip, *Appl. Phys. Lett.*, 61, 8, pp.1003-1005 (1992)
- [6] J. Nakamura, M. Miyamoto, S. Hasaka, and H. Koyanagi: High-density thermomagnetic recording method using a scanning tunneling microscope, *J. Appl. Phys.*, 77, 2, pp.779-781 (1995)
- [7] A. Sato, S. Momose, and Y. Tsukamoto, Nanometer-scale recording, erasing, and reproducing using scanning tunneling microscopy, *J. Vac. Sci. Technol.*, B13, 6, pp.2832-2836 (1995)

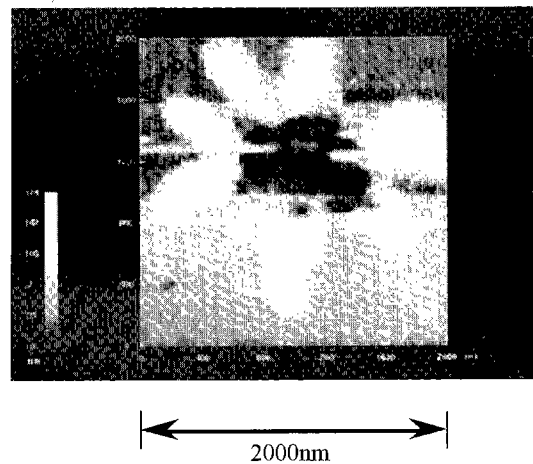


Fig. 4. An example of topographic image of DLC film after application of -5V to 800nm x 800nm area.

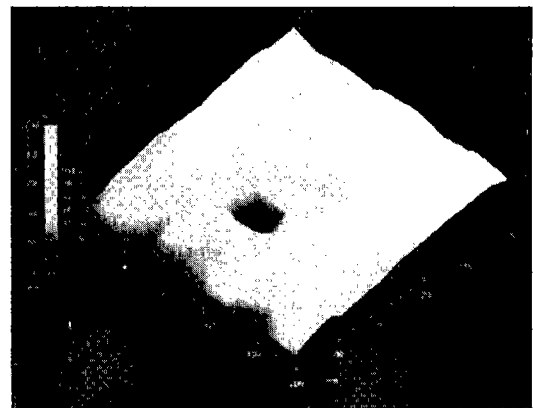


Fig. 5. Topographic image of DLC film after application of voltage pulse (-15V) with the width of 50ms. Scanning area is 200nm x 200nm.

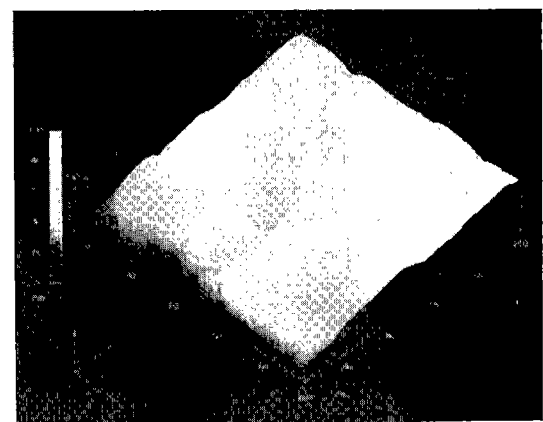


Fig. 6. Topographic image of DLC film after application of voltage pulse (-15V) with the width of 10ms. Scanning area is 200nm x 200nm.

- [8] T. Hirano, T. Furuhashi, and H. Fujita: Dry-released nickel micromotors with low-friction bearing structure, IEICE Trans. Electron, E78-C, 2, pp.132-138 (1995)
- [9] S. Umemura, Y. Andoh, S. Hirono, T. Miyamoto and R. Kaneko: Nanoindentation and nanowear tests on amorphous carbon films, Phil. Mag. A74, 5, pp.1143-1157 (1996)
- [10] P.J. Rabe, S. Buchholz and A.M. Ritcey: J. Vac. Sci. & Technol., A8, pp.679 (1990)
- [11] W. Mizutani, J. Inukai, and M. Ono: Jpn. J. Appl. Phys., 29, pp.L815 (1990)
- [12] S. Hosaka, H. Koyanagi and A. Kikukawa: Nonometer recording on graphite and Si substrate using an atomic force microscope in air, Jpn. J. Appl. Phys., 32, pp.L464-L467 (1993)

**Reizo Kaneko** (Non-Member) He received the M.S. and Ph.D. degrees in mechanical engineering from Kyoto University in 1964 and 1973, respectively. He joined the NTT Electrical Communications Laboratories in 1964 and since then he had been engaged in research and development on magnetic and optical recording apparatuses and research on surface science and technology including microtribology. Since 1996, he has been a Professor at Wakayama University.



**Shigeki Tsuchitani** (Member) He received the M.S. degree in material physics from Osaka University in 1979 and the Ph.D degree in electronic physics from Tokyo Institute of Technology in 1994. Since 1979, he had been working for Hitachi Ltd. and engaged in research and development on sensors. In 1996, he joined the Dep. of Opto-Mechatronics at Wakayama University.



His research interests include microsensors, microactuators and nanomachining technologies.

**Yoshinori Nakano** (Non-member) He received B.S. degree in opto-mechatronics from Wakayama University in 2000. He is now studying for his M.S. degree as a graduate student of Wakayama University.



**Yoshihiro Imagawa** (Non-member) He received B.S. degree in opto-mechatronics from Wakayama University in 2000. He is now studying for his M.S. degree as a graduate student of Wakayama University.



**Shigeru Hirono** (Non-member) He received M.S. and Ph.D. degrees in applied physics from Nagoya University in 1977 and 1988, respectively. He joined the NTT Electrical Communications Laboratories in 1977 and since then he had been engaged in research on magnetic films for recording media, quantum effect devices and protective films using ECR sputtering method. Since 1998, he has been developing ECR sputtered protective films for practical use in Advanced Film Technology Inc.

