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DEVELOPMENT OF PHOTOELECTRON-ASSISTED CHEMICAL VAPOR DEPOSITION

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Abstract

We developed a photoelectron-assisted chemical vapor deposition (PACVD) that can deposit an ultra-thin perfluoropolyether (PFPE) film on a diamond-like carbon (DLC) surface. The DLC surface with a 1 nm-thick PFPE film deposited by the PACVD showed a low surface energy. The surface also showed a low adhesion force that was caused by the low surface energy. We confirmed that the PFPE/DLC surface deposited by the PACVD has the potential to improve the areal density of hard disk drives.

1. Introduction

Functional surfaces with advanced physical or chemical functions have been recently studied, and various products using functional surfaces have been developed. Investigation of high-functional surfaces also leads to the development of new products and a new research field. The functional surface is related to manufacturing of items such as hard disk drives (HDDs), cars, solar cells, displays, and charge devices. Thus, functional surface manufacturing processes that have a low cost and uniformity in a large area of functional surface are needed. Highly sensitive analysis technology for the functional surface is also required.

A functional surface with a very thin film, similar to monolayer thickness and a very low surface energy are required for the magnetic disks in HDDs. A perfluoropolyether (PFPE) liquid lubricant film that is approximately 1 nm thick is generally formed on the DLC (diamond-like carbon) protective film of the magnetic disks. The coverage and orientation of the lubricant film influence the magnetic disk performance. These PFPE coating films are also generally used in touch screen surfaces to prevent dirt from the fingerprints from sticking to the surface. Thus, the density and orientation of the coating film influence its anti-fouling function.

This paper reviews the development of the photoelectron-assisted chemical vapor deposition (PACVD) that can deposit a lubricant film on a diamond-like carbon (DLC) surface. Tani et al. previously found that the photoelectrons emitted from a DLC surface that was

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irradiated by an ultraviolet (UV) light dissociated the hydroxyl end groups of PFPE lubricant molecules, and the dissociated end groups chemically adsorbed to the DLC surface (Fig. 1) [1]. The PACVD is a new deposition method that is applied with this reaction mechanism that includes photoelectrons, lubricant molecules, and the DLC surface. The fluorocarbon film used to lubricate magnetic disks (high water contact angle of $> 90^\circ$, thickness of only a few nanometers) cannot be deposited by plasma, chemical vapor, or ion beam-assisted deposition. Karis et al. investigated a new lubricant film based on the ion beam-assisted deposition of fluorinated monomers [2]. The water contact angle of this film was less than 90° . However, Leezenberg et al. modified the chemical surface of amorphous carbon films by venting with fluorinated gases after sputtering [3]. The water contact angle in their study was less than 70° .

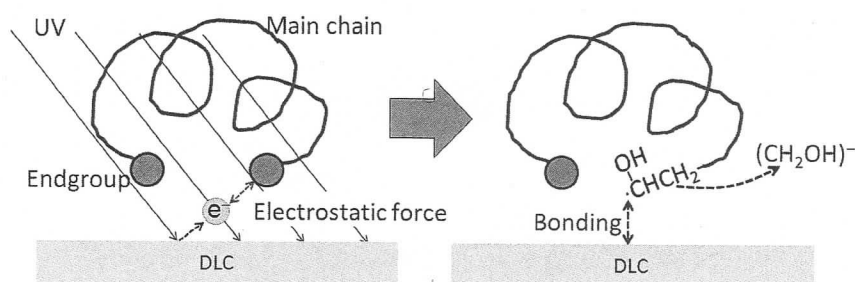


Fig. 1. UV bonding mechanism resulting from the dissociation of the hydroxyl end groups caused by photoelectron capture [1]

The PACVD process we developed may not completely decompose the PFPE precursor because glow discharge plasma is not generated. In our previous studies, we found that the photoelectron emissions accelerated by the electric field applied to the disk surface increase the chemical bonded ratio [4]. The PACVD is based on a mechanism where the bias voltage accelerating the photoelectron emissions and the photoelectrons partially dissociates the lubricant molecules (Fig. 2). Therefore, the lubricant film can chemically bond with the DLC surface to form an ultrathin PFPE/DLC hybrid coating. We show preliminary data on the effect of the bias voltage under UV irradiation for the bonded ratio and the tribological properties of magnetic disks [5]. The dissociation process of the lubricant molecules under

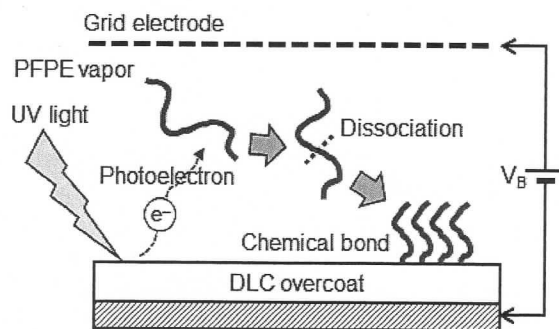


Fig. 2. Schematic image of the photoelectron-assisted chemical vapor deposition (PACVD) process depositing an ultrathin PFPE/DLC hybrid overcoat [6]

UV irradiation is analyzed as a relationship between the bias voltage and the surface energy using time-of-flight secondary ion mass spectrometry (TOF-SIMS). We also show the evaluation results of the PFPE film deposited on the DLC surface using PACVD. The chemical structure of the deposited film is analyzed using X-ray photoelectron spectroscopy (XPS) and TOF-SIMS. In addition, the friction and pull-off forces are measured using a pin-on-disk tester. The head-media clearance and the read/write characteristics are also measured on disk surfaces that are fabricated using the PACVD process [6].

2. Bias voltage effect under UV irradiation

Figure 3 shows the experimental setup. UV light was irradiated through a quartz window and a grid electrode onto the disk surface. The inner and outer chambers were purged using nitrogen gas without oxygen. The UV lamp was a low-pressure mercury lamp with wavelengths of 185 nm and 254 nm. The light intensity of the 254 nm wavelength was approximately 5 mW/cm^2 on the disk surface. The magnetic disk sample was a glass substrate that was 65 mm in diameter, in which a magnetic film was deposited using sputtering. An approximately 3-nm-thick DLC protective film was deposited on it by chemical vapor deposition. The lubricant films were formed by dipping for 3 min in solutions made by dissolving the lubricants, Fomblin Z-tetraol (Solvey Co., Ltd. Brussels, Belgium) and ADOH (Moresco Co., Ltd. Kobe, Japan). Z-tetraol has hydroxyl end groups, while ADOH has a cyclo-triphosphazene end group with an m-trifluoromethyl-phenoxy single end group. Kasai and Wakabayashi [7] indicated that the cyclo-triphosphazene end group of ADOH was more sensitive to the photoelectron chemical reaction than the hydroxyl end groups. Thus, ADOH should show a higher bonded ratio after UV irradiation than Z-tetraol because the cyclo-triphosphazene end groups are easily dissociated by photoelectrons. The chemical-bonded thickness was obtained as the lubricant thickness after washing the mobile- and hydrogen-bonded lubricant off through rinsing in ethanol. The bonded ratio was defined as the ratio of the lubricant thickness after the rinse and the initial thickness.

The bonded ratio of Z-tetraol slightly increased with the photoelectron-assisted UV irradiation. However, the bonded ratio of ADOH drastically increased with UV irradiation. This result is in agreement with previously published results, where the cyclo-triphosphazene

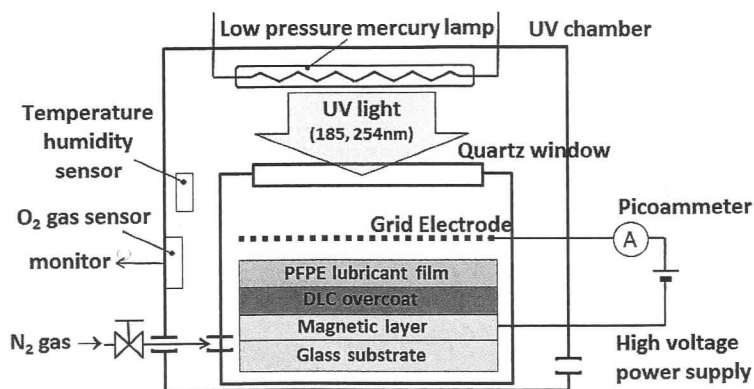


Fig. 3. Schematic image of the experimental setup [5]

end group of ADOH was more sensitive to photoelectron chemical reaction than the hydroxyl end groups in the other lubricants [7].

We evaluated the lubricant depletion using the pin-on-disk test with laser heating at 300°C. The pin-on-disk tester that we developed was used in this experiment, with laser irradiation at the contact area through a glass pin [5]. The results are shown in Figure 4. ADOH depletion decreased as the duration of the UV irradiation increased, and ADOH depletion with a bias voltage of -1800 V was shallower than that without the bias voltage. The photoelectron-assisted UV irradiation process with a bias voltage of -1800 V had an average of 0.3 Å less depletion than the normal UV irradiation without a bias voltage. However, the bonded ratios of the disks after UV irradiation for 300 s were almost 100%. Compared with Z-tetraol, ADOH showed a small depletion probably because ADOH with a cyclo-triphosphazene end group has a higher thermal stability than Z-tetraol. Thus, the photoelectron-assisted UV irradiation was effective in reducing the lubricant depletion. We then compared the bonding behavior of both lubricant films that were subjected to normal and photoelectron-assisted UV processes using TOF-SIMS.

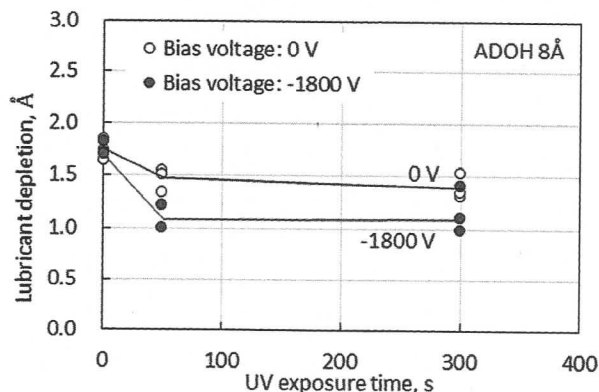


Fig. 4. Lubricant depletion of ADOH treated by UV irradiation with and without a bias voltage [5]

Figure 5 shows the fragments of the decomposed end groups in the TOF-SIMS negative spectrum of the lubricant film without UV irradiation. The fragments of the end groups with different numbers of trifluoromethyl-phenoxy functions were observed. The trifluoromethyl-phenoxy function of the cyclo-triphosphazene end groups was easily dissociated by

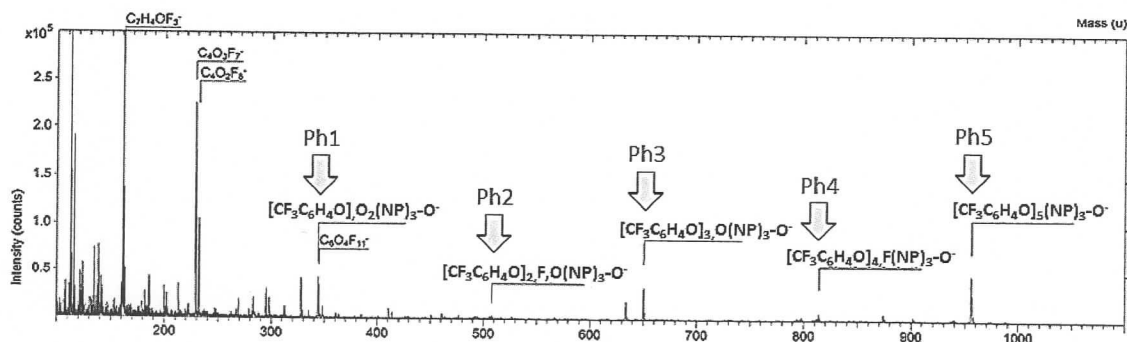


Fig. 5. Negative spectrum of the decomposed cyclo-triphosphazene end groups [5]

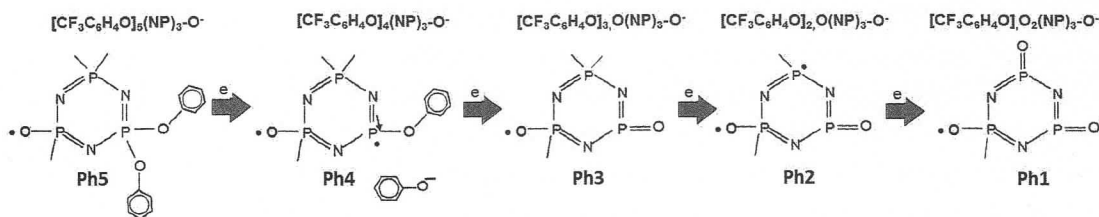


Fig. 6. Schematic image of the sequential decomposition of a cyclo-triphosphazene end group caused by the photoelectron dissociation of trifluoromethyl-phenoxy [5]

photoelectron capture. Thus, the end group was estimated to sequentially decompose (Fig. 6). Increasing the adsorption strength of the end groups to the DLC surface is also possible if end group decomposition progresses. The UV irradiation with a bias voltage proceeded with the decomposition of the cyclo-triphosphazene end groups because the photoelectron emission was increased by this process. The dangling bond at the end group increases as the dissociation progresses if the cyclo-triphosphazene end group progressively dissociates. Consequently, decomposition of the cyclo-triphosphazene end group proceeded through the photoelectron-assisted UV irradiation. The depletion of the lubricant film treated by UV irradiation with a bias voltage after laser heating was shallower than that of the film subjected to the normal process. These results suggested the following: the bias voltage under UV irradiation accelerated the photoelectron emissions; the photoelectrons might be able to dissociate the PFPE molecules in the vapor phase; and the dissociated molecules chemically adsorbed to the DLC surface.

3. Photoelectron-assisted chemical vapor deposition

Figure 7 schematically illustrates the PACVD experimental setup. A UV excimer light was irradiated through a quartz window and a grid electrode onto the disk surface [6]. A DC bias voltage was applied to the grid electrode and the disk was grounded to the earth. The PFPE monomer vapor was injected into the vacuum chamber by the evaporator, and the PFPE

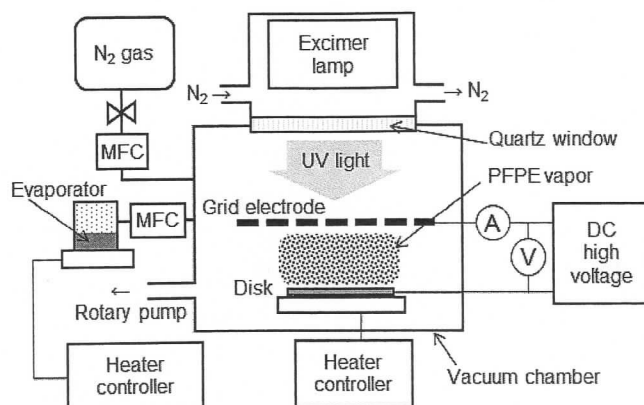


Fig. 7. Schematic image of the experimental setup. UV light is irradiated to the disk surface in the vacuum chamber. The bias voltage is applied between the grid electrode and the disk surface to accelerate the photoelectron emissions from the DLC surface [6].

vapor flow into the vacuum chamber was controlled by a mass flow controller. The gas pressure in the vacuum chamber was controlled to 170 Pa, and the bias voltage was 300 V. The grid electrode was hexagonal. The distance between the electrode and the disk surface was 4 mm. The PFPE monomer material used was Galden HT-170, which is a well-known heat transfer fluid manufactured by Solvay (Brussels, Belgium). The material has a boiling point of 170°C, a vapor pressure of 107 Pa, and an average molecular weight of 760 Da. For reference, we also prepared UV-treated and dip-coated Z-tetraol disks.

Figure 8 shows a plot of the dispersive and polar components of the surface free energy, which were derived from the measured contact angles, as a function of the deposited film thickness. The dispersive component of the HT-170 film was comparable to that of the Z-tetraol film. However, the polar component of HT-170 was much lower than that of Z-tetraol. The polar component of the HT-170 film when the film was more than 10 Å thick was a few millijoules per square meter because the HT-170 film chemically adsorbed to the DLC surface, and the bonded ratio was almost 100%.

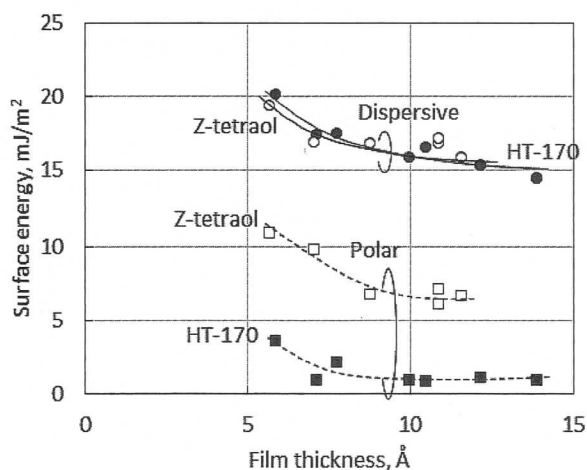


Fig. 8. Surface free energy as a function of the deposited HT-170 film thickness compared to those of the dip-coated and UV-treated Z-tetraol [6]

Figure 9 shows the C1s spectrum of the 6.6 Å-thick HT-170 film measured by XPS. Only the CF and CF₂ components were observed in the Z-tetraol spectrum. However, the CF, CF₂, and CF₃ components were observed in the HT-170 spectrum. The CF₃ component in the HT-170 spectrum originated from the chemical structure of HT-170 because Z-tetraol does not have a CF₃ component in its chemical structure. Figure 10 presents the TOF-SIMS negative mass spectrum of the HT-170 deposited film. The deposited HT-170 film showed some fragments derived from the original HT-170 structure in the negative mass spectrum. Therefore, the deposited HT-170 film showed a chemical structure similar to that of the HT-170 molecules. The PFPE/DLC hybrid film also had a large CF₃ component.

The friction force and pull-off force were measured using our pin-on-disk microtribo-tester, and the results are shown in Figure 11. The pull-off force was observed at the separation of the pin and the disk surface with Z-tetraol. The pull-off force on the Z-tetraol lubricant film was 0.7 mN. However, the pull-off force was not observed on the HT-170 film. The adhesion

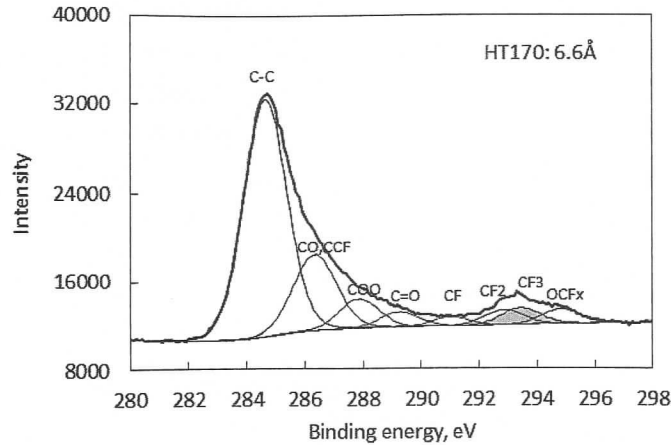


Fig. 9. Cls spectra of the HT-170 films measured by XPS

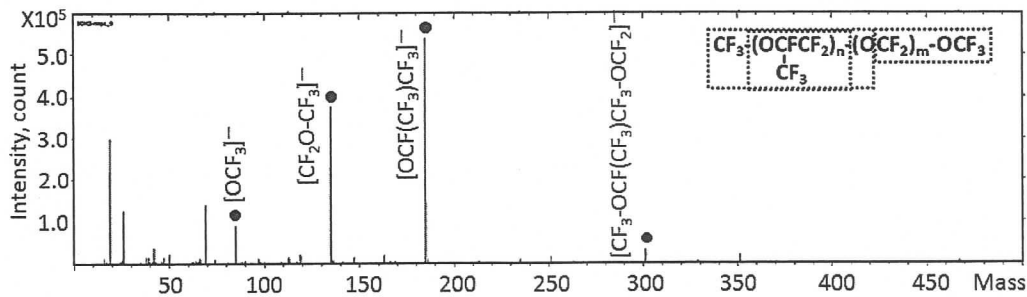


Fig. 10. Negative ion mass spectrum of the deposited HT-170 film measured using TOF-SIMS [6]

force depends on the surface free energy of the contact between the two surfaces [8] and the meniscus between the pin-and-disk surfaces affects the pull-off force. Thus, the pull-off force could not be observed in this study because the HT-170 film was completely chemically bonded, and the polar surface energy was very low.

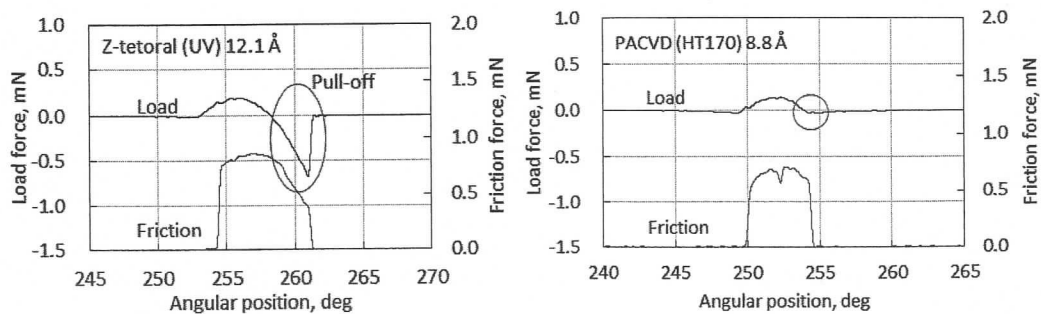


Fig. 11. Load force and friction force measured by our developed pin-on-disk tester: (a) 12.1 Å-thick Z-tetrol and (b) 8.8 Å-thick HT-170 film

The HT-170 film deposited using PACVD showed a high chemical bonded ratio, an excellent low polar surface energy, and no pull-off force. The deposited film structure included

the PFPE vapor material. The deposited film surface was rich with the CF_3 component. The deposited film also included the HT-170 chemical structure. In addition, we evaluated the head-media clearance and the read/write performance of the deposited film by the component tests using the spin stand [10]. The head-media clearance of the deposited film was larger than that of the reference disk by approximately 4 mW. Thus, the HT-170 film improved the clearance between the slider and disk surfaces. This improvement was because the stable flying of slider above the disk surface was not disturbed by the pull-off force at the slider-disk contact and because the monolayer thickness of the HT-170 film was thinner than that of the actual disk. The read/write performances of the HT-170 film was also better. Thus, the read/write characteristics were improved in the disk with a HT-170 film deposited by PACVD. This may be because the spacing between the magnetic layer of the disk and the magnetic head was reduced by the increased clearance between the slider and disk surfaces. Therefore, the PFPE/DLC surface deposited using PACVD has the potential to improve the areal density of HDDs.

4. Conclusion

We developed a PACVD that can deposit an ultra-thin PFPE film on a DLC surface. The DLC surface with a 1 nm-thick PFPE film deposited by the PACVD showed a low surface energy and a very low adhesion force caused by the very low surface energy. We confirm that the PFPE/DLC surface deposited using PACVD has the potential to improve the areal density of HDDs.

Acknowledgments

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