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Effect of Heat Treatment Temperature on PFPE Molecules Bonded on DLC Surface

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Based on the demand of extremely increased area density for magnetic data storage, the contact recording systems have been proposed, in which stronger and thinner hard coatings and lubricant films for the head disk interface (HDI) are desired. In this study, two lubrication methods, i.e., the vacuum vapor deposition and dip-coating methods are evaluated and compared in order to satisfy the demands from the HDI development. Perfluoropolyether (PFPE) is applied to the diamond-like carbon (DLC) surface. The advantage of the vacuum vapor deposition is to prevent contamination of the DLC surface from the atmosphere because of no exposed samples to the atmosphere. In contrast, the advantage of dip-coating method is to thicken the bonded layer of the PFPE by heat treatment. We discuss the adsorption mechanism between the PFPE molecules and DLC surface for each method. In addition, a simple reaction model based on the Arrhenius equation is developed and compared to the experimental results. We concluded that the reaction will be dominated by covalent bonds and hydrogen bonding. Furthermore, the reaction model can well express the experimental results. The remarkable destruction of the DLC film by the heat treatment are not seen in the samples heat treated at a temperature from 353 to 423 K while the remarkable destruction are seen in the samples treated from 423 to 473 K.

Keywords: diamond-like carbon (DLC), perfluoropolyether (PFPE), Arrhenius equation, vacuum vapor deposition, dip-coating

1. Introduction

The storage density of hard disk drives (HDDs) has increased with a decrease in the flying height between the head and disk. At the head-disk interface (HDI) in HDDs, in order to decrease the serious tribological damage originating from the intermittent or continuous contact between the head and disk, a diamond-like carbon (DLC) overcoat with about a 2-3 nm thickness is deposited on the magnetic layer of the magnetic disk, then an ultrathin hydroxyl-terminated perfluoropolyether (PFPE) film as a monolayer or even less is coated on the DLC surfaces[1,2)], where the monolayer means the lubricant film fully covering the DLC surface except for physically adsorbed molecules. It is well known that the PFPE film with a strong adhesion and bonding to the DLC surface is effective in reducing the friction and wear of HDI[3)]. In addition, a thicker bonded layer of the PFPE molecules invites a higher wear resistance against the intermittent or continuous contact between the head and disk[4)]. Vacuum vapor deposition of the PFPE film can effectively produce the thickest bonded PFPE film layer, which will be a monolayer, because some pollution of the DLC surface originating from the atmosphere can be avoided[5)]. For vacuum vapor deposition, the PFPE film can be lubricated on the DLC surface without exposure to the atmosphere, therefore, contamination from the atmosphere does not affect the adsorption between the PFPE molecules and the active sites of the DLC surface during the lubrication process. On the other hand, in the traditional dip-coating method for PFPE lubrication, the heat treatment process can effectively increase the thickness of the bonded layer of the PFPE film[6-11)]. In this study, the PFPE bonded layer is formed on the DLC surface as a function of the heat treatment time by the dip-coating method and compared to that by the vacuum vapor deposition method. In addition, a reaction model

based on the chemical kinetics is developed and compared to the experimental results.

2. Experimental setup

DLC films deposited on a cut silicon wafer with an RMS roughness of nominally 0.4 nm are prepared using the plasma chemical vapor deposition (PCVD) method. A CH_4 and N_2 gas mixture with a flow ratio of 20 vol% N_2 is used as the precursor. The thickness of the DLC film is about 200 nm. Commercial Fomblin Zdol (molecular weight MW = 4000) from the SOLVAY SOLEXIS is used as the PFPE lubricant. Fomblin Zdol is a normal chain polymer with two hydroxyl end groups. PFPE molecules are coated on the DLC surface by the vacuum vapor deposition and traditional dip-coating methods. For the vacuum vapor deposition method, PFPE molecules are evaporated at 423 K under vacuum condition (base pressure is about ~10^{-4} Pa) and absorbed on the DLC surface without exposure to the atmosphere. In contrast to the dip-coating method, the DLC sample is lubricated with PFPE molecules by dipping the DLC sample into a 5 vol% PFPE solution which is dissolved by HFE-7100DL solvent. After dipping, the samples are heated in the range from 353 to 473 K for several time periods. In order to rinse away the physically absorbed molecules, both samples made by the vacuum vapor deposition and dip-coating methods are washed using the HFE-7100DL solvent, therefore the bonded PFPE molecules just remain on the DLC surface.

3. Results

3.1. XPS measurements

X-ray photoelectron spectroscopy (XPS) measurements were used in this study. The typical carbon core level spectra (C1s) of the DLC and PFPE are shown in Fig. 1. The typical DLC peak at around 285 eV can be observed for all samples, while the typical PFPE peak at around 294 eV can be observed for samples with the PFPE molecules. The PFPE peak increases with an increase in the heat treatment time. This means that the bonded layer of the PFPE for dip-coating is thinner than the monolayer of the PFPE, and the heat treatment process accelerates the adsorptions of the PFPE molecules on the DLC surface. In contrast, the sample made by vacuum vapor deposition accomplishes the maximum intensity of the PFPE peak as shown in the figure. In comparison with the bonded layer of the PFPE by dip-coating, the bonded layer made by the vacuum vapor deposition will be similar to the PFPE of monolayer. Based on the results of the XPS measurements, the thicknesses, h, of the PFPE film fixed on the DLC surface were calculated using the following equation[12]:

$$h = \lambda \times \ln\left(\frac{I_{PFPE}}{I_{DLC}} + 1\right) \quad (1)$$

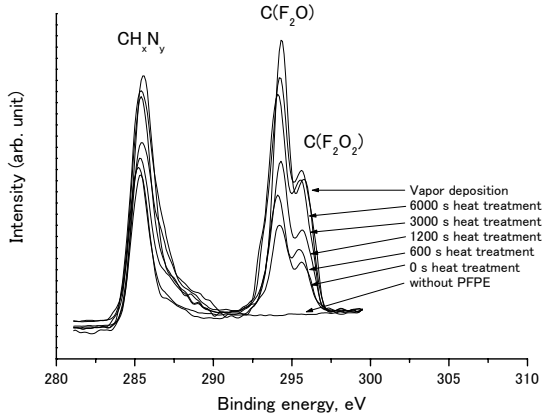

Fig. 1 Results of XPS measurements for samples after rinsing with solvents

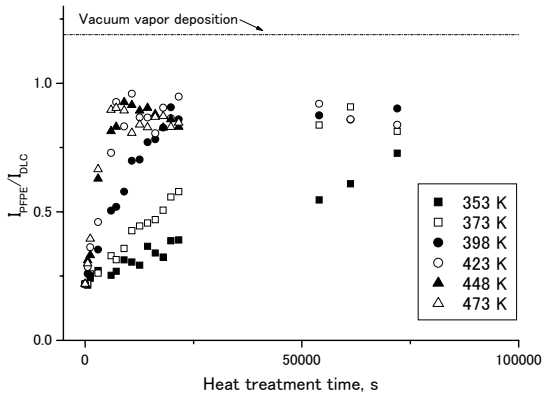

Fig. 2 Relation between I_{PFPE}/I_{DLC} ratio and heat treatment time for samples after rinsing with solvents

where λ is the mean free path of the carbon atom, and I_{PFPE} and I_{DLC} are the area intensities of the PFPE and DLC peaks determined from the XPS measurements, respectively. We must note that when the film thickness is less than a monolayer thickness, h_{max}, the ratio of the surface coverage, θ, related to the PFPE molecules covering with the DLC surface can be denoted, h/h_{max} because the XPS measurement is an optical analysis and the results indicate the mean value that depended on the X-ray spot area. In addition, θ can also denote N/N_{max}, where N_{max} is the number of all the active sites on DLC surface and N is the number of the active sites bonded to the PFPE molecules. The relations between the I_{PFPE}/I_{DLC} ratio and heat treatment time are shown in Fig. 2. From the figure, the ratio increases with the increase in the time for all the treatment temperatures, and then the ratio settled at around 0.9 and does not go beyond this value. The maximum film thickness calculated from equation (1) is about 1.96 nm for the vacuum vapor deposition in this study.

3.2. Arrhenius plot

Based on these results that the heat treatment

process accelerates the bonding of the PFPE molecules on the DLC surface, the behavior will be dominated by the bonding kinetics. On the basis of the experimental results, a kinetic model based on first-order reactions will be initially evaluated in this study. The model assumes that bonding of PFPE molecules only occurs from the mobile molecules and no decomposition of the bonded molecules occurs. Since the bonding of the PFPE molecules only occurs from the monolayer covering the DLC surface, the kinetic equation using the change in the mobile fraction of the monolayer, C_M, is shown below, where t and k are the heat treatment time and a reaction rate constant, respectively.

$$-\frac{dC_M}{dt} = k \times C_M \tag{2}$$

Note that C_M can denote (1-θ). The following equation can be obtained from the integral of equation (2), where C_{M0} (=1-θ_0, where θ_0 is the initial surface coverage when t=0) is the initial condition when t is equal to zero, i.e., no heat treatment.

$$\ln\left|\frac{C_M}{C_{M0}}\right| = \ln\left|\frac{1-\theta}{1-\theta_0}\right| = -kt \tag{3}$$

On the basis of equation (3), a plot of $ln|(1-\theta)/(1-\theta_0)|$ vs. t yields a straight line with a slope of k for $t > 0$. From the temperature dependence of k, the activation energies for bonding can be obtained via the Arrhenius equation as shown below.

$$k = A \cdot e^{-(E_a/RT)} \tag{4}$$

where A and E_a which are individual constants, are the frequency factor and the activation energy, respectively. R and T are the gas constant and heat treatment temperature, respectively. From equations (3) and (4), the relation between θ and the Arrhenius parameters are shown below.

$$\ln\left|\frac{1-\theta}{1-\theta_0}\right| = -A \cdot e^{-(E_a/RT)} \cdot t \tag{5}$$

On the other hand, $|(1-\theta)/(1-\theta_0)|$ can be expressed using the experimental results and Eq. (1) as follows,

$$\left|\frac{1-\theta}{1-\theta_0}\right| = \frac{1-N/N_{\max}}{1-N_0/N_{\max}} = \frac{1-h/h_{\max}}{1-h_0/h_{\max}} = \frac{\ln\left[\left\{1+\left(I_{PFPE}/I_{DLC}\right)_{\max}\right\}/\left\{1+\left(I_{PFPE}/I_{DLC}\right)\right\}\right]}{\ln\left[\left\{1+\left(I_{PFPE}/I_{DLC}\right)_{\max}\right\}/\left\{1+\left(I_{PFPE}/I_{DLC}\right)_0\right\}\right]} \tag{6}$$

$(I_{PFPE}/I_{DLC})_0$ is the initial value when t is equal to zero, i.e., the experimental results without any heat treatment are applied. $(I_{PFPE}/I_{DLC})_{\max}$ means the intensity ratio of the monolayer.

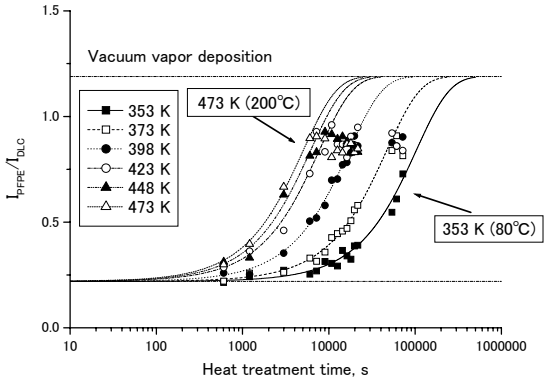

Fig. 3 Relation between experiments and analytical curve

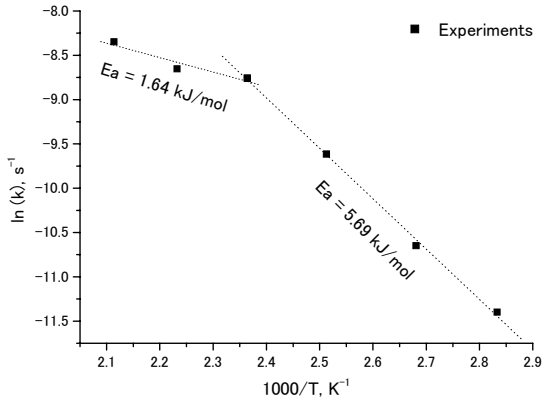

Fig. 4 Relation between ln k and 1000/T

4. Discussion

In this study, I_{PFPE}/I_{DLC} from the vacuum vapor deposition is substituted for $(I_{PFPE}/I_{DLC})_{\max}$ as the 'experimental' maximum value. Using equations (5) and (6), the results of the calculations based on the kinetic model are shown by the several lines drawn through the experimental data points in Fig. 3. From the figure, the calculations can well express the experimental results for all temperature when the values of I_{PFPE}/I_{DLC} are less than about 0.9. This means that the bonding is accelerated by the heat treatment process. One of the features of bonding will be PFPE bonding which occurs when a hydrogen atom is transferred from the hydroxyl end to a dangling bond on the DLC surface[13]. In addition to bonding, hydrogen bonding between the hydroxyl end of the PFPE and an amine terminated sites on the DLC surface may occur because the desorption energy between the hydroxyl end and an amine terminated sites is higher than that between the hydroxyl end and an oxidized site on the DLC surface[5,6]. In this study, the amount of covalent bonding and hydrogen bonding were not quantitatively determined, therefore, a quantitative analysis for the covalent bonds and the

hydrogen bonding must be a future study in order to clarify these features. On the other hand, disagreement between the calculations and the experimental results occur at the values around 0.9. One of the reasons for this will be some oxidation and contamination of the DLC surface. It will be difficult to fully achieve a thicker bonded layer using the dip-coating method because exposure to air oxidizes the DLC surface that partially forms oxidized carbonaceous species and invites some contamination chemisorbed on the DLC surface. The vacuum vapor deposition can avoid the oxidation and contamination of the DLC surface, therefore, the maximum intensity of the PFPE peak occurs as shown in Figs. 1, 2 and 3.

Fig. 4 shows a plot of ln k vs. 1000/T from the experiments. From this figure, two slopes due to the straight plot can be obtained. The calculated E_a from 353 to 423 K and from 423 to 473 K are 5.69 kJ/mol and 1.64 kJ/mol, respectively. Waltman et al. described in their paper that E_a of the same PFPE molecules (MW is different) obtained from their study is about 15.1 kJ/mol (3.6 kcal/mol) for bonding[14,15]. Stirniman et al. showed the relation between the activation energy and the molecular weight of the same PFPE molecules, where E_a is about 170 kJ/mol in their paper[16]. Since the activation energy should be an individual constant due to the experimental conditions such as the DLC film thickness, roughness of the film, and PFPE MW, it will be difficult to simply compare our results and their results, however, the differences in the nitrogen incorporation into the DLC film and the initial thickness of the PFPE during heat treatment will have significant effects on the activation energy. On the other hand, the two calculated E_a values from the figure means that the bonding kinetics for each temperature range will be different. For the experiments in this study, there is no destruction of the sample heat treated at a temperature from 353 to 423 K while the destruction of the DLC film treated at a temperature from 423 to 473 K occurs as shown in Fig. 5. PFPE droplets, a broken DLC film and bare silicon surface exist with disorder as shown in the figure, where the surface properties are investigated by microlaser Raman spectroscopy. This means that PFPE molecules and the DLC film may have some chemical reactions at more than 423 K, and then the DLC film itself is destroyed by the internal stress of the film. In order to obtain the change in the weight of the samples as a function of the heat treatment, especially the heat treatment temperature, thermogravimetric analyzer measurement was accomplished in this study. The samples were heated from room temperature to 873 K with a 0.83 K/s heating rate. Fig. 6 shows the results of the measurement. From the figure, the changes in the weight of the samples for only the DLC and the lubricated DLC with rinsing are very small, which will be caused by the graphitization of the DLC film, however, the weight of the sample for the lubricated DLC without rinsing changes obviously at more than

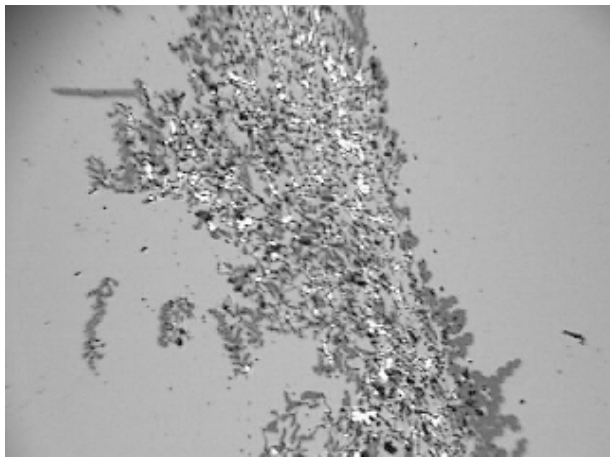

Fig. 5 Optical microscope image of sample treated at 448 K for 6000 s

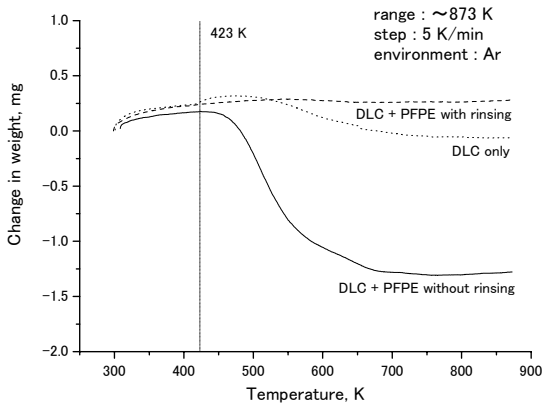

Fig. 6 Results of thermogravimetric measurement

423 K of the temperature. The evaporation of mobile lubricant must have effects on the weight decrease, however, the DLC film also decomposed and destroyed similarly as shown in Fig. 5 in case of the sample with DLC + PFPE without rinsing. The weight decrease will be caused by the decomposition of the DLC and the PFPE, i.e., the chemical reaction between the DLC and the PFPE. On the other hand, the samples of only the DLC and the lubricated DLC with rinsing after the measurement did not have the destruction as shown in Fig. 5. We must note that the effect of the difference in the thermal expansion coefficients of the DLC film and the Si substrate on the destruction will be small in comparison to that of the chemical reaction. Chen et al. described in their paper that the observed decomposition temperature for a 2000 MW PFPE is 429 K with a 0.2 K/s heating rate[17]. The 4000 MW PFPE without fractional treatment is used in this study, therefore, the used PFPE molecules will have a wide MW range due to the normal distribution. Consequently, the lower MW PFPE actively desorbs during the heat treatment of more than 423 K and then the desorbed PFPE will undergo some chemical reactions with the DLC film. Kasai has described in his

paper that PFPE molecular chains are prone to undergo an intramolecular disproportionation reaction which is catalyzed by Lewis acid (electron-deficient) sites[18,19]. Based on his studies of the PFPE decomposition on the surface of Al_2O_3, the PFPE decomposition occurs by an intramolecular disproportionation reaction in which Lewis acid site on the Al_2O_3 interacts with two oxygen atoms flanking a monomer -CF_2- unit within the PFPE backbone. It will be possible to consider that the Lewis acid sites on the DLC surface will play the role of a catalyst against the PFPE molecules as in the previous description. To confirm the catalysis, it should be investigated in a future study.

5. Conclusion

In this study, the effect of the heat treatment time and temperature on the bonded phase of the PFPE on the DLC surface was surveyed and the bonding mechanism of the PFPE on the DLC surface was modeled. The conclusions are as follows,

1. The calculations can well express the experimental results for all temperature when the values of I_{PFPE}/I_{DLC} are less than about 0.9. In contrast, disagreement between the calculations and the experimental results occur at the values around 0.9. One of the reasons for this will be some oxidation and contamination of the DLC surface for dip-coating method.
2. The remarkable destruction of the DLC film by the heat treatment are not seen in the samples heat treated at a temperature from 353 to 423 K while the remarkable destruction are seen in the samples treated from 423 to 473 K. In addition, the change in the weight occurs obviously at more than 423 K when the PFPE lubricated sample without rinsing. This will be caused by the decomposition of PFPE mobile molecules which are the lower molecular weight.

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