Quantitative Analysis of Surface Functional Groups on the Amorphous Carbon in Magnetic Media with XPS Preceded by Chemical Derivatization

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In thin film magnetic recording media, the carbon protective layer and the outermost lubricant layer have a significant influence on the tribological properties. It is thought that the functional groups on the surface of the carbon influence the adsorption of the lubricant. The present study describes the identification and quantification of the functional groups on the surface of magnetic thin film media based on an X-ray photoelectron spectroscopy (XPS) preceded by chemical derivatization. The number of functional groups on the surface of the carbon protective layer was obtained from the ratio of the fluorine and carbon in the XPS spectrum. Gas-phase chemical modification was found to be preferable as a pretreatment for surface analysis, and the number of carbonyl, hydroxy, and carboxylic acid groups were directly determined. The number of hydroxy group was higher immediately after deposition, and the carbonyl group, of which the concentration rapidly increased with exposure time to air, became the most abundant. Both groups improved the affinity of the lubricant and will probably lead to a better lubricity.

Magnetic recording technology is the most economic form of storage for many applications. The advantage of magnetic storage is that the storage density is increasing at a very rapid rate. Recently, with the introduction of thin film media and a giant magneto-resistive head, storage densities are increasing at a rate of 100% per year. The storage density in hard disks reached 250 Mbit mm^{-2} during development.[1] Diamond-like carbon (DLC) is applied over the Co-based magnetic layer as a smooth protective layer, and one to two monolayers of perfluoro-polyether (PFPE) is used as a lubricant. The tribological properties of ultra-thin films have attracted considerable attention, because these films can dramatically influence the durability of recording media, which limits the storage density before the magnetic limit is achieved. The rapidly increasing storage density will soon require carbon overcoats of only 2 nm and a lubricant of less than 1 nm to achieve the above recording density. In order to ensure the tribological properties and lifetime of magnetic recording system, it has been thought that the lubricant molecule to a certain degree should bind to the disk surface to avoid spin-off from the rapidly rotating disks, depletion caused by head-media interactions, or simple displacement by adsorbed water or airborne organic compounds.[2] PFPEs are commonly used as media surface lubricants because of their relatively high chemical stability. When PFPE is applied to a carbon overcoat layer, a part of the PFPE becomes bonded to the surface through the functional groups. The interaction of the PFPEs and the carbon surface has been discussed in several papers. Merchant et al. have reported that the boundary layer lubricants are chemically adsorbed on the carbon layer, while the outermost lubricant molecules are physically bonded to each other.[3] Ruhe et al. have proposed that the esterification reaction between the hydroxy end groups of DOL and the carboxylic acid groups on the carbon is the bonding mechanism.[4] Not only the lubricant film properties but also the surface interaction with the carbon layer becomes a matter of importance in this region. However, the nature of the carbon surface at the magnetic thin film media and especially the quantitative analysis of the functional groups on the surface have not been thoroughly investigated.

The chemical composition of the carbon surface is normally analyzed by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Characterization of the surface functional groups, such as carbonyl and hydroxy, on glassy carbon electrodes is performed using Raman spectroscopy. A fluorescein derivative is usually the label for hydroxy groups[5] and dinitrophenylhydrazine for labeling surface C=O groups.[6]

Direct quantitative analysis of the functional groups attached to the surface, such as hydroxy, carbonyl, and carboxylic acid, is relatively difficult even with high-resolution XPS, because the penetration depth is greater than the thickness of the outermost functional group and airbone contaminants contribute to these signals. As a consequence, the signal due to the functional group contributes only a small fraction to the C–O carbon signal in the narrow region XPS.

To help overcome this problem, curve-fitting procedures, which attempt to decompose the XPS spectrum into a collection of individual peaks, are utilized. XPS has been used to characterize oxides on carbon, most commonly by deconvolution of the C_{1s} in high-resolution spectra. Sherwood et al. have determined surface coverage of alcohol, carbonyl, and carboxylate groups.[7–10] Total oxide coverage of carbon fiber was generally 10–15% with the principal species being alcoholic (3–7%) and carbonyl (3–5%) groups.

An alternative approach to the curve fit analysis is chemical speciation via derivatization using fluorinated XPS tag molecules. Numerous studies have described derivatization reac-

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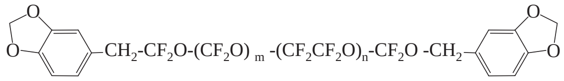
Table 1. Molecular Structure of the Perfluoropolyether

Perfluoropolyether	Molecular structure
DOL	$HO–CH_2–CF_2O–(CF_2O)_m–(CF_2CF_2O)_n–CF_2O–CH_2–OH$
AM	

tions, which increase the specificity of XPS for the analysis of polymer and glassy carbon surfaces,[11–18] and most of the oxidized carbon groups, such as hydroxy, carbonyl, and carboxyl, are found to specifically react with special reagents. Derivatization reagents, which contain a unique elemental tag, can readily be identified in subsequent XPS analysis. In principle, these reagents should selectively and analytically react with only the intended functional group. The elemental tag should have a favorable photoelectric cross-section and should be stable during analysis. Most of these reactions should preferably occur in the gas phase to avoid problems, such as residual solvent on the surface and swelling of the substrate, experienced in the XPS measurements. Nakayama et al. have succeeded in quantitating the surface composition by gas-phase chemical modification.[19] Several methods to generate standard polymer surfaces can be envisioned. Wide varieties of commercial polymers are available and could help characterize the reaction specificity. For example, poly(vinyl alcohol) might be useful to evaluate reactions with an alcohol function, poly(vinyl methyl ketone) with a carbonyl function, and poly(acrylic acid) with a carboxylic acid function.

The present study represents an endeavor to develop a methodology to identify and quantitate carbon–oxygen containing functional groups on the surface of the carbon protective layer in order to gain a better understanding of the origin of the tribology problems associated with these surface materials composition. The thickness of the carbon layer (10 nm) is very thin, and the oxygen content is relatively small compared to previous studies. Therefore, a specific derivatization reaction in gas phase was employed prior to the XPS analysis, in order to tag the surface functional groups with fluorine that could be detected and quantitated in the XPS survey scan.

Experimental

Tape Samples and Lubricant Labeling Reagents. An metal-evaporated (ME) tape sample was similar to commercially available tape, in which the magnetic layer, a Co thin film of thickness 150 nm, is formed on poly(ethylene terephthalate) (PET) tape by the oblique incident deposition method. A 10-nm thick carbon protective layer was then prepared by chemical vapor deposition following.[20] This magnetic tape was produced in a vacuum chamber, then exposed to the atmosphere for the purpose of lubricant coating.

We examined two types of PFPE lubricants, of which the terminal group was a hydroxy for DOL and a piperonyl group for AM. They are widely used as a lubricant for commercial magnetic thin film media. Their molecular structures are summarized in Table 1. Each lubricant was deposited on a carbon layer by the dip-coating method at the concentration of 0.05 wt % in a fluorinated solvent, of which boiling point is 60 °C. The chemical structure of the solvent is a linear fluoropolyether end-capped with a hydrogen atom, $HF_2–(OC_2F_4)_p–(OCF_2)_q–CF_2H$. Both the fluorinated lubricants and the solvent were purchased from Solvey Solexis K.K. and used without further purification. The physically adsorbed lubricant was removed by rinsing the same fluorinated solvent. The thickness of the lubricants was also measured by XPS.[21]

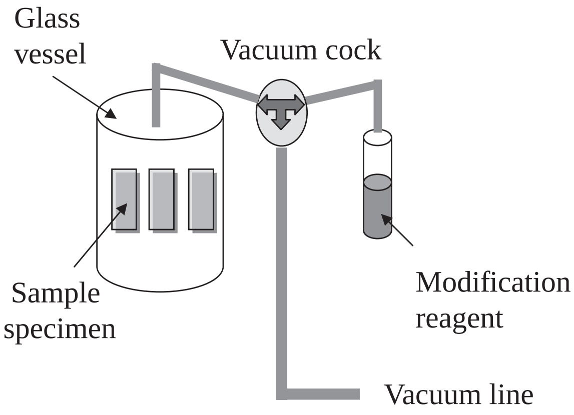


Fig. 1. Chemical modification system.

Labeling Reagents and Preparation of Standard Model Sample. Pentafluorophenylhydrazine (PFPH), trifluoroacetic anhydride (TAA), and 2,2,2-trifluoroethanol (TFA), which were used as labeling reagents, were purchased from Aldrich Chemical Co. as reagent grade and used without further purification.

Poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), and poly(vinyl methyl ketone) (PVMK) were used as model sample polymers and dissolved in water, acetone, and ethanol, respectively, deposited on the PET substrate, and then allowed to air-dry under clean bench conditions at 80 °C for more than 1 day prior to the XPS analysis.[16] These samples were checked by XPS and IR and shown to be adequate reference samples.

Preparation and Derivatization of Carbon Layer and Standard Polymer. Derivatization reactions were focused on the identification of carbon oxidation state that is hydroxy, carbonyl, carboxylic acid groups after exposure to the atmosphere, and were carried out under identical conditions. All reactions were conducted in vacuo to avoid any decomposition with the water in the air. The chemical modification system scheme is shown in Fig. 1. After the completion of the chemical modification, the 2 L reaction chamber was re-evacuated in order to remove extra reagents. The yield of the reaction was estimated from the model reactions of standard polymers treated under the same conditions.

The reaction formulas for the gas chemical modifications are summarized in Fig. 2. Hydroxy groups, carbonyl groups, and carboxylic acid groups were derivatized with TFAA, TFE, and PFPH, respectively. The labeling of the hydroxy group of PVA with TFAA needed to be done at room temperature for 5 min to obtain saturation. Esterification of the surface carboxyl groups of PAA, saturated with TFE reagent, was performed at 60 °C for 4 h. Dicyclohexylcarbodiimide (DCC) was added as a catalyst according to the amount of the TFE injections. Gas-phase PFPH was reacted with the carbonyl group of PVMK at 80 °C. The reaction

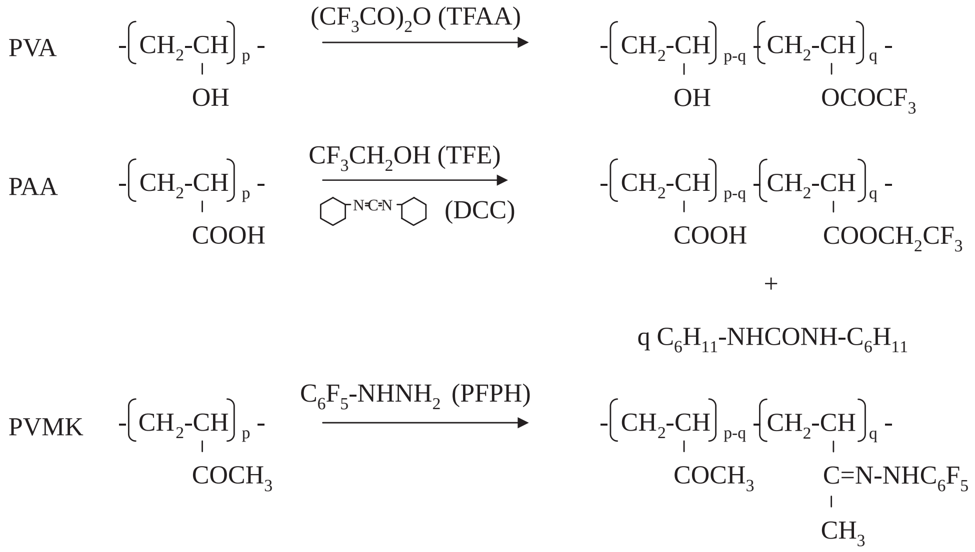


Fig. 2. Reagents and chemical reactions used for surface modification of the standard polymer.

was performed under saturated conditions for 2 h. The concentration of TFAA was about 1.8×10^{-3} mol L^{-1}, TFE was 3.6×10^{-3} mol L^{-1}, and PFPH was 0.1×10^{-3} mol L^{-1}.

XPS Measurements. Spectra of the tape samples were obtained before and after the chemical modification. An ULVAC-PHI ESCA5400MC spectrometer was used with a Mg Kα X-ray source (1253.6 eV). The pressure in the sample chamber was maintained at or below a vacuum of 1×10^{-7} Pa, and a take-off angle of 45° from the surface was used. An X-ray power of 50 W (14 kV, 3.5 mA) was used to minimize the damage to the fluorine-containing PFPEs and labeling reagents due to the X-ray irradiation.

The fluorine content was also measured by XPS, and the film thickness was calculated.[22–25] The C, F, and O signals were recorded and used to calculate the thickness of PFPE based upon Beer's law attenuation of the underlayer signals by the overlying layers. Specifically, it is assumed that the signals originating below any given interface are attenuated by $\exp(-d/\lambda)$, where d is the thickness of the overlayer and λ is the electron escape depth, which was presumed to be 3.0 nm in this case. There are several assumptions and simplification in this formulation. The most significant are: the substrate and overlayers are flat and smooth, and their interfaces are abrupt. In the interest of simplicity and ease of exchange of this method among laboratories, these seem reasonable.

Contact Angle Measurements. Equilibrium advancing contact angles were measured in the ambient atmosphere. Drops were applied to the surface using a fine capillary tube. The angle on both sides of the drop was measured and the average taken. The surface energies were divided into the dispersive and polar components,[26] which were calculated by extension of Fowkes' equation from the contact angles with water and diiodomethane.[27]

Results and Discussion

Change in Surface Energy. The change in the nature of the outermost carbon surface with time is distinguishable by the wettability, and the surface energy was calculated from contact angle measurements. The polar component seems to be related to the number of functional groups on the carbon surface and rapidly increased within the first 10 days, as can be seen in Fig. 3. It became saturated at about 14 mJ m^{-2}. On the other hand, the dispersive component gradually decreased to 34 mJ m^{-2}, possibly due to airbone contaminants.

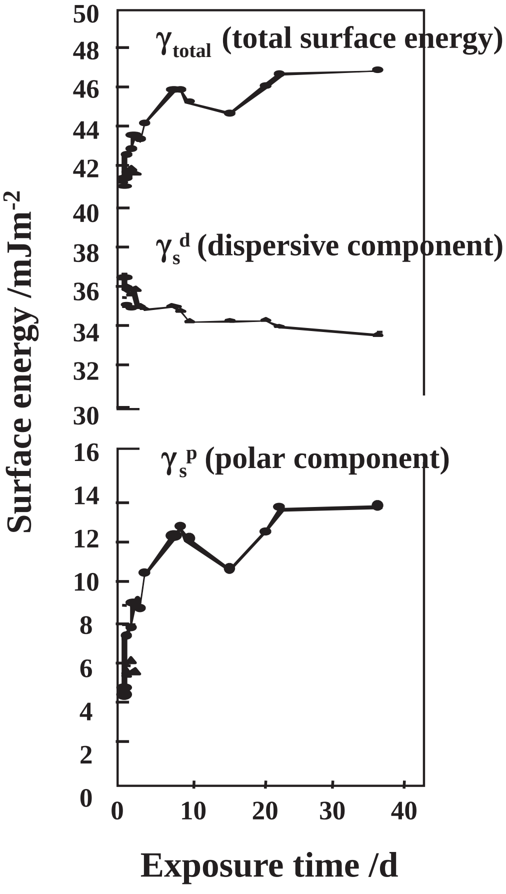


Fig. 3. Change in surface energy on the CVD carbon film as a function of exposure time.

XPS Measurement. The XPS result of the samples upon standing is shown in Fig. 4. The O/C atomic ratio rapidly increased with exposure to the atmosphere during the first 5 days and tended to saturate, which shows the same tendency as the

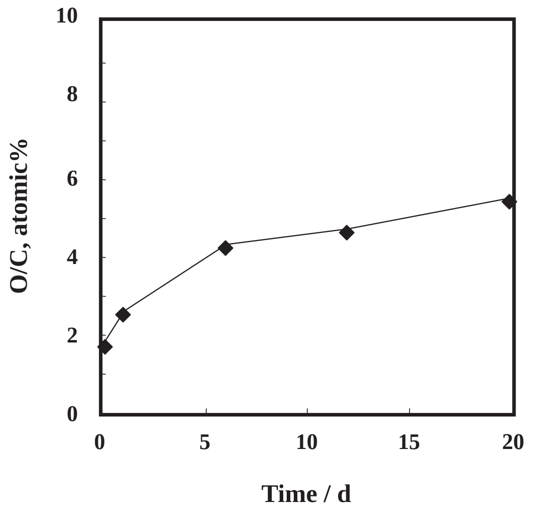


Fig. 4. Change of the oxygen/carbon atomic ratio with time of exposure to the atmosphere.

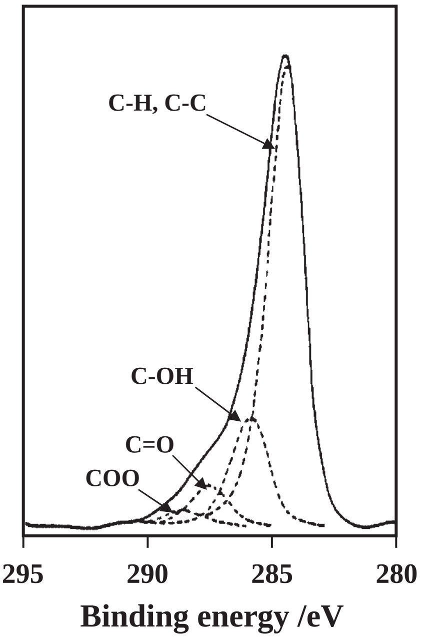


Fig. 5. C_{1s} XPS spectrum of amorphous carbon surface.

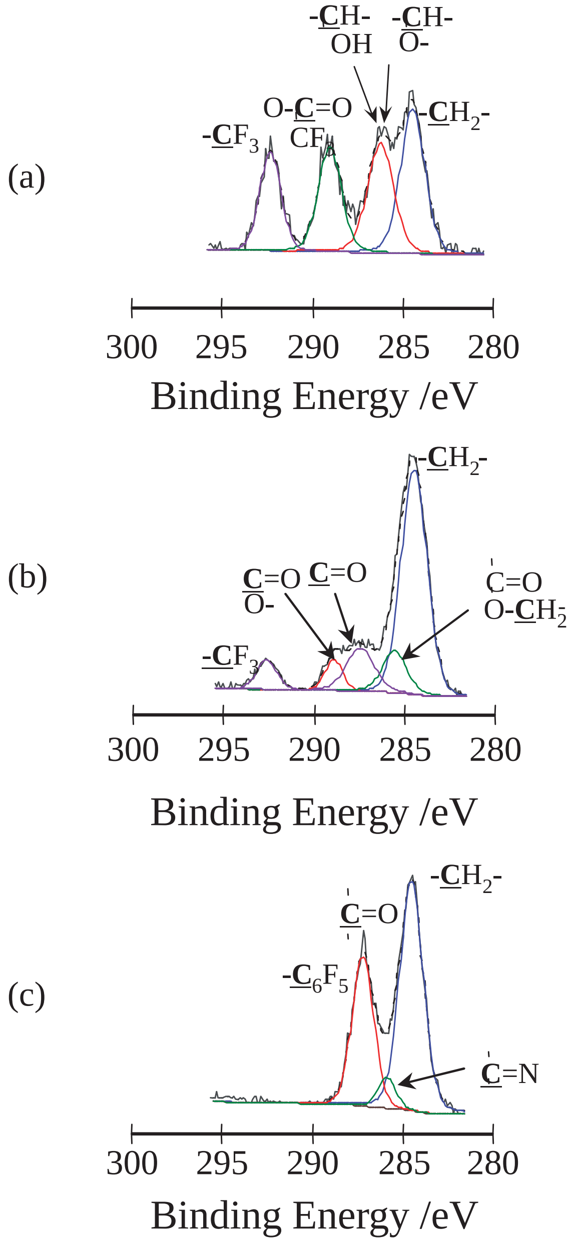


Fig. 6. C_{1s} XPS spectra of standard polymers after gas-phase chemical modification. (a): Poly(vinyl alcohol) after modification with TFAA. (b): Poly(acrylic acid) after modification with TFE and DCC. (c): Poly(vinyl methyl ketone) after modification with PFPH.

surface polarity. The oxidization of the carbon surface seems to increase gradually. In this case, the increase in the oxygen content is mainly caused by air oxidation, and we could ignore the contamination from the air by comparison with a silicon wafer under the same condition.

The carbon 1s (C_{1s}) XPS spectrum of the surface is shown in Fig. 5. However, the identification of oxidized carbon atoms, such as hydroxy, carbonyl, and carboxylic acid groups, after exposure to the atmosphere is relatively difficult even using high-energy-resolution XPS. To help overcome this problem, curve-fitting procedures were utilized to decompose the XPS spectrum into a collection of individual peaks, Fig. 5. Although these useful deconvolution procedures provide information, they are not specific enough to probe the quantitative structure of the oxidized carbon surface. Therefore, we examined which type of oxidation reaction occurred in this process by the chemical derivatization method.

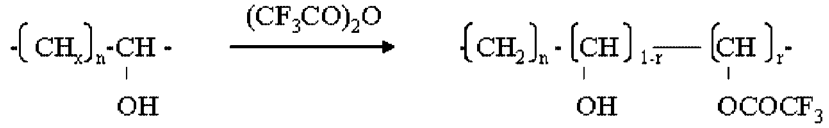
Chemical Derivatization Method with Standard Polymers. In order to measure the actual chemical composition of the carbon surface, a surface modification technique using fluorinated tag molecules was employed. The number of surface functional groups was obtained from the ratio of the fluorine and carbon signals in the XPS of the modified surface.

Figure 6 shows the C_{1s} XPS spectrum of the gas-phase reaction of standard polymers treated with the labeling reagents. We confirmed the reaction selectivity of the reagent and every functional group beforehand using the references.[11,15,16] TFAA reacted with only the hydroxy groups, while the reaction with

Table 2. XPS Raw Data and the Reaction Yield for the Each Experiment to Calculate Functional Group Concentration on the Carbon Surface

		Day									
		0[a)]		1		6		12		20	
OH	F_{1s}	931	1067	995	957	1003	895	963	1053	963	1781
	C_{1s}	7228	7316	6814	6814	6446	6492	6590	6344	6734	13570
	r	0.68		0.69		0.62		0.60		0.59	
	R_{OH}	1.9	2.2	2.2	2.1	2.6	2.3	2.5	2.8	2.5	2.3
COOH	F_{1s}	127	323	388	395	243	284	375	373	426	432
	C_{1s}	6792	7512	7450	7610	6796	6670	7413	7168	6952	6632
	r	0.55		0.79		0.80		0.72		0.99	
	R_{COOH}	0.3	0.8	0.7	0.7	0.4	0.5	0.7	0.7	0.6	0.7
CO	F_{1s}	751	627	1011	970	1802	1877	1918	1908	2031	1995
	C_{1s}	7152	7424	6898	6996	6334	6285	6462	6342	6554	6496
	r	0.98		0.98		0.96		0.97		1.0	
	R_{CO}	1.1	0.8	1.5	1.4	3.4	3.6	3.6	3.6	3.6	3.6

a) We measured each experiment twice and averaged the results.



Scheme 1. Derivatization reaction of hydroxy group with TFAA on the surface.

carboxylic acid could be ignored.[19,28] PFPH reacted with both carbonyl and carboxyl groups.[29] However, TFE reacted only with carboxylic acid by catalyzing with DCC, whereas it did not react with PVA at the same condition.[19,30] Thus, we could distinguish the amount of the carbonyl group.

The yield of the reaction was estimated from the C_{1s} XPS spectrum in Fig. 6a, which shows the spectrum of PVA after modification with TFAA. The component of the C_{1s} XPS spectrum at binding energy of 286.1 eV was assigned to hydroxide carbon (A) and the trifluoro-substituted carbon (B) was assigned to 292.9 eV. Therefore, the yield of the reaction was calculated as (B)/(A) in Fig. 6a.

To understand qualitatively the vertical nature, that is, surface to sub-surface, of the modified polymer surface, we determined angular-dependent ratio of C_{1s} and F_{1s} peak intensity, and F_{1s}/C_{1s} did not depend on the angle, which suggests that the relative distribution of these elements is similar within the XPS sampling depth.[11]

For the esterification of surface carboxyl groups with TFE and DCC reagents, the yield was estimated from the trifluoro-substituted carbon (292.9 eV)/carboxyl carbon (288.9 eV) in Fig. 6b.

Gas-phase PFPH was reacted with PVMK at 80 °C. The peak of the pentafluorophenyl group and the unreacted carbonyl group were overlapped and could not be separated. Therefore, the yield of the reaction was estimated by comparing the C=N carbon at 285.7 eV and the peak at 287.5 eV in Fig. 6c. In this case, the unreacted carbonyl group did not appear even in the shoulder peak at 287.5 eV in Fig. 6c, that means the reaction yield was almost 100%. We conducted these model modification reactions for the each tape sample to ensure the reaction yield, which are summarized in Table 2.

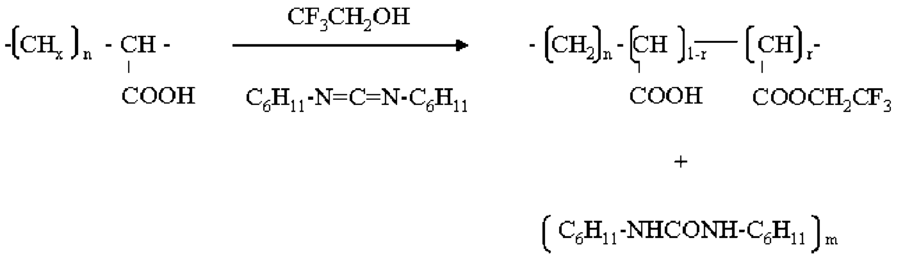
Quantification of Functional Groups of Amorphous Carbon Surface by Gas-Phase Chemical Modification. The atomic ratio of the functional group carbon to all the detected carbon atoms in a sample (R_f) is estimated by the following formulas based on the reaction scheme for each derivatization (Scheme 1).

The atomic ratio of the hydroxy group carbon to all the carbon atoms detected in a sample (R_{OH}) is estimated from Eq. 1.

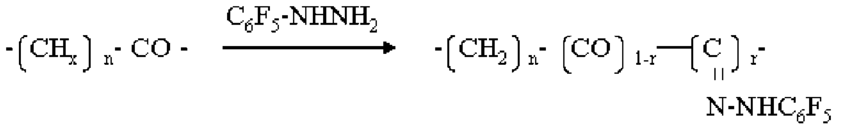
$$\begin{aligned} R_{OH} = \frac{[C_{1s}]^{OH}}{[C_{1s}]} &= \frac{{}_{\text{unreacted}}[C_{1s}]^{OH} + {}_{\text{reacted}}[C_{1s}]^{OH}}{[C_{1s}]_{\text{after}} - [C_{1s}]^{COO} - [C_{1s}]^{CF3}} \\ &= \frac{(1/r)[C_{1s}]^{CF3}}{[C_{1s}]_{\text{after}} - 2[C_{1s}]^{CF3}} \\ &= \frac{(1/3)[F_{1s}]\cdot(1/k_{F1s})\cdot(1/r)}{[C_{1s}]_{\text{after}} - 2/3[F_{1s}](1/k_{F1s})} \\ &= \frac{[F_{1s}]}{(3k_{F1s}[C_{1s}]_{\text{after}} - 2[F_{1s}])r} \end{aligned} \tag{1}$$

where $[F_{1s}]$ is the F_{1s} peak area of the sample, $[C_{1s}]$ is the C_{1s} peak area before modification, $[C_{1s}]_{\text{after}}$ is the C_{1s} peak area after modification, ${}_{\text{unreacted}}[C_{1s}]^{OH}$ and ${}_{\text{reacted}}[C_{1s}]^{OH}$ are unreacted and reacted hydroxy carbon with TFAA respectively, k_{F1s} is the relative sensitivity factor of $[F_{1s}]$, and r is the reaction yield. $[C_{1s}]^{CF3}$ and $[C_{1s}]^{COO}$ are same and calculated by the F_{1s} peak area using the relative sensitivity factor k_{F1s}. The value of r was estimated from a model reaction of PVA treated under the same reaction condition in the former section. k_{F1s} is the relative sensitivity factor of F_{1s} and was 3.38 for this case; therefore, R_{OH} was calculated using $[C_{1s}]_{\text{after}}$ and $[F_{1s}]$, which were measured by using XPS after the derivatization reaction (Scheme 2).

R_{COOH} was estimated by Eq. 2. ${}_{\text{unreacted}}[C_{1s}]^{COOH}$,



Scheme 2. Derivatization reaction of carboxyl group with TFE on the carbon surface.



Scheme 3. Derivatization reaction of carbonyl group with PFPH on the carbon surface.

${}_{\text{reacted}}[\mathrm{C}_{1s}]^{\mathrm{COOH}}$, and $[\mathrm{C}_{1s}]^{\mathrm{CF3}}$ were calculated using the $[\mathrm{F}_{1s}]$, r, and k_{F1s}. $[\mathrm{C}_{1s}]^{\mathrm{DCC}}$ is the peak area of residual DCC. The ratio of the residual DCC derivative (m) is the ratio of residual DCC derivatives adsorbed on the surface, which is estimated from the analysis of the O_{1s} peak of urea ($[\mathrm{O}_{1s}]^{\mathrm{NHCONH}}$) and carboxyl group ($[\mathrm{O}_{1s}]^{\mathrm{COO}}$) which were observed at 531.7 and 532.2 eV, respectively, after the modification reaction (not shown here).[19] m was 0.1 in this case. The constants 2 and 13 in the second term of the denominator of (2) are used to exclude the carbon atoms that come from the TFE and DCC derivative in the sample.

$$\begin{aligned}
R_{\mathrm{COOH}} &= \frac{[\mathrm{C}_{1s}]^{\mathrm{COOH}}}{[\mathrm{C}_{1s}]} \\
&= \frac{{}_{\text{unreacted}}[\mathrm{C}_{1s}]^{\mathrm{COOH}} + {}_{\text{reacted}}[\mathrm{C}_{1s}]^{\mathrm{COOH}}}{[\mathrm{C}_{1s}]_{\text{after}} - 2[\mathrm{C}_{1s}]^{\mathrm{CF3}} - [\mathrm{C}_{1s}]^{\mathrm{DCC}}} \\
&= \frac{(1/r)[\mathrm{C}_{1s}]^{\mathrm{CF3}}}{[\mathrm{C}_{1s}]_{\text{after}} - 2[\mathrm{C}_{1s}]^{\mathrm{CF3}} - [\mathrm{C}_{1s}]^{\mathrm{DCC}}} \\
&= \frac{(1/3)[\mathrm{F}_{1s}]\cdot(1/k_{\mathrm{F1s}})\cdot(1/r)}{[\mathrm{C}_{1s}]_{\text{after}} - 2/3[\mathrm{F}_{1s}](1/k_{\mathrm{F1s}}) - 13m(1/3k_{\mathrm{F1s}})[\mathrm{F}_{1s}]} \\
&= \frac{[\mathrm{F}_{1s}]}{\{3k_{\mathrm{F1s}}[\mathrm{C}_{1s}]_{\text{after}} - (2 + 13m)[\mathrm{F}_{1s}]\}r} \qquad (2)
\end{aligned}$$

R_{CO} was estimated by using Eq. 3 based on the Scheme 3. ${}_{\text{unreacted}}[\mathrm{C}_{1s}]^{\mathrm{CO}}$ and ${}_{\text{reacted}}[\mathrm{C}_{1s}]^{\mathrm{CO}}$ in the numerator are the peak area of unreacted and reacted carbonyl carbon, respectively, and $[\mathrm{C}_{1s}]^{\mathrm{C6F5}}$ is the peak area of the carbon of pentafluorophenyl group and was also calculated by using the $[\mathrm{F}_{1s}]$, r, and k_{F1s}.

$$\begin{aligned}
R_{\mathrm{CO}} = \frac{[\mathrm{C}_{1s}]^{\mathrm{CO}}}{[\mathrm{C}_{1s}]} &= \frac{{}_{\text{unreacted}}[\mathrm{C}_{1s}]^{\mathrm{CO}} + {}_{\text{reacted}}[\mathrm{C}_{1s}]^{\mathrm{CO}}}{[\mathrm{C}_{1s}]_{\text{after}} - [\mathrm{C}_{1s}]^{\mathrm{C6F5}}} \\
&= \frac{(1/5)[\mathrm{F}_{1s}]\cdot(1/k_{\mathrm{F1s}})\cdot(1/r)}{[\mathrm{C}_{1s}]_{\text{after}} - 1/5[\mathrm{F}_{1s}](1/k_{\mathrm{F1s}})} \\
&= \frac{[\mathrm{F}_{1s}]}{(5k_{\mathrm{F1s}}[\mathrm{C}_{1s}]_{\text{after}} - [\mathrm{F}_{1s}])r} \qquad (3)
\end{aligned}$$

We examined the change in the functional group, such as the hydroxy, carboxyl, and carbonyl at the CVD carbon overcoat surface with exposure to air by using the chemical modification. The samples that we exposed to air at regular time intervals were placed in the vacuum glass vessel to react with TFAA, TFE + DCC, or PFPH, and then, XPS measurements were conducted.

The results of chemical derivatization/XPS analysis are shown in Fig. 7. Figure 7a is the modification of hydroxy group with TFAA, Figure 7b is of carbonyl with PFPH, and Figure 7c is of carboxyl with TFE. After the XPS measurements, the amount of the each functional group with exposure time was confirmed. A fairly large quantity of hydroxy group existed immediately, whereas the number of carboxyl group was small. We confirmed the increase in the amount of carbonyl groups with exposure time.

The functional group concentrations of each samples calculated from the equations stated above and the XPS raw data are summarized in Table 2. The average concentration of the functional groups for two experiments as a function of exposure time to air is shown in Fig 8. The carbon surface was hydroxylated immediately just after contact with the atmosphere; however, it did not significantly change. The increase in the carbonyl groups was compared to that of the other functional groups at the beginning and saturated within 5 days. The quantity of the carboxyl-carbon was the lowest among the three functional groups, and the quantity was also constant during the examination period. Surface oxidation occurred rapidly during the initial 5 days, and the total number of functional groups nearly doubled.

Adsorption of Lubricant. It is known that when PFPEs with functional end groups are applied to the carbon overcoat, some part of the PFPE becomes "bonded" such that it cannot be removed by rinsing with solvents. This type of lubricant is effective for depletion due to the centrifuged force of a high rotation speed and/or drying problems. The "unbonded" part is washed out with solvent, which is widely believed to be free to flow across the surface to replenish the lubricant in areas where it has been depleted by head-media contact.[2,3]

Figure 9 shows the change in the lubricant thickness on a carbon surface before and after solvent washing. We used the tapes, which were exposed to the atmosphere for different lengths of time. The formation of the lubricant film is a spontaneous process caused by a decrease in the free energy of the solid surfaces and lubricant molecule adsorption. The heat of adsorption of the lubricants on rubbing surfaces can be taken as a measure of the strength of attachment of the lubricant to

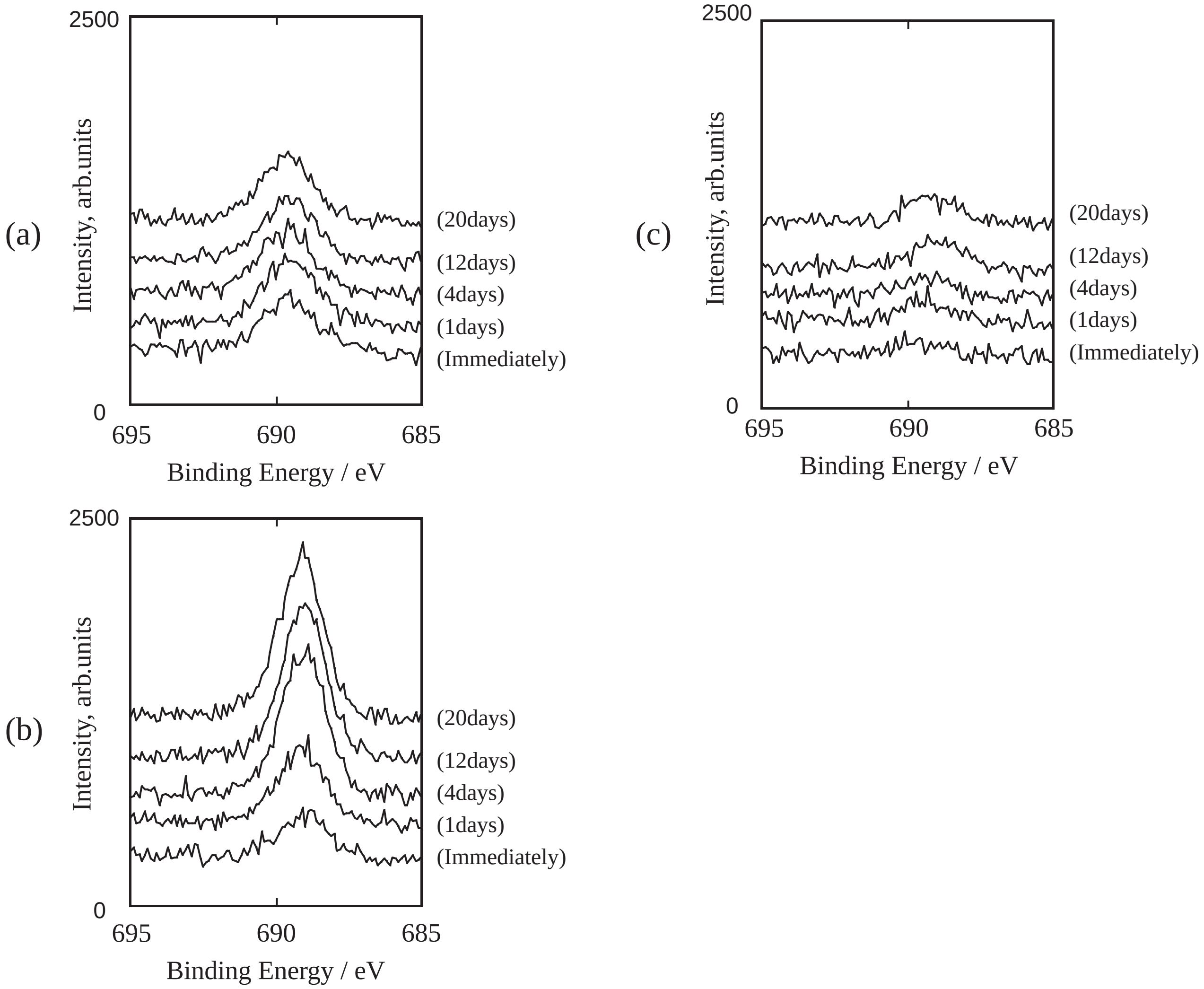


Fig. 7. Changes in F_{1s} XPS spectra of the tape samples of the each functional group with exposure time after chemical derivatization. (a) Hydroxy group, (b) carbonyl group, and (c) carboxyl group.

the surface. The heat of adsorption of the PFPE upon the carbon powder for DOL and AM were 3.7 and 5.0 mJ g^{-1}, respectively.[31] Therefore, the thickness is greater for the latter than for the former.

The total lubricant thickness of the hydroxy-terminated DOL and the piperonyl-terminated AM increased with exposure time and was nearly saturated within 5 days. The lubricant was deposited by the dip-coating method at the same concentration; therefore, the affinity of the lubricant on the surface became stronger with surface oxidation. The total amount of the deposited lubricant immediately after exposure to air is postulated to mainly interact with the hydroxy group on the surface, because the mechanism of interaction with the PFPE and the carbon surface involves hydrogen bonding.[32,33] It was almost half compared with the sample after the oxidation was completed in both cases in spite of the different polar end groups. Both PFPEs developed an affinity to the carbonyl group, which increased with exposure time. The amounts of adsorbed lubricant was mostly proportional to the total number of functional groups on the surface, as shown in Fig. 8. PFPEs have a polar fluoroether group in the backbone polymer chain. The bonding of the ethers to the carbon surfaces occurs through the donation of electrons from the lone pairs of the oxygen atom, and it is weak due to the strong electron-withdrawing effect of the fluorine atoms.[34] This is why end polar groups are mainly responsible for adsorption. The surface oxidation mechanism is different for the hydroxy group and carbonyl group; however, both lubricants show a similar adsorption tendency, which implies that both the hydroxy group and carbonyl group affect the lubricant adsorption. In order to control the lubricant thickness during fabrication, we determined favorable length of time for the coating.

The white circles and squares in Fig. 9 show the "bonded" lubricant thickness. The bonded lubricant ratio was almost one-third at all stages of oxidation in spite of the different lubricant thicknesses. From a chemical point of view, the accurate meaning of a "bonded" lubricant is not obvious; therefore, we can not discus it in detail in this paper.

Conclusion

A quantitative surface analysis of the carbon protective layer for magnetic recording media was conducted. By using high resolution XPS, we showed that the O/C atomic ratio rapidly increased with exposure to the atmosphere and tended to satu-

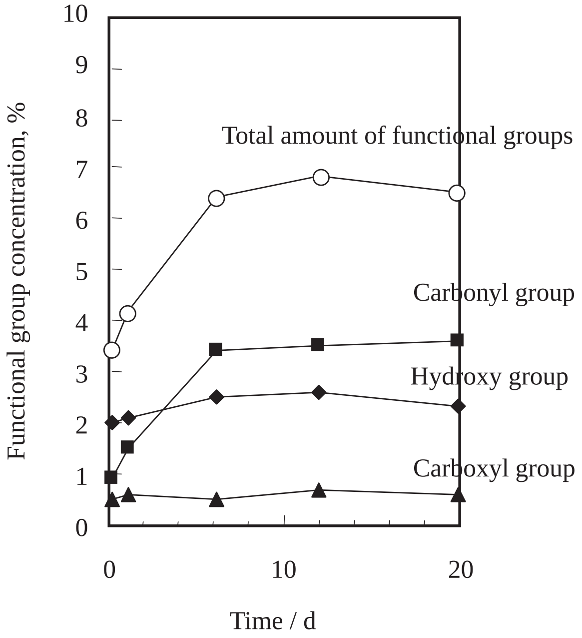


Fig. 8. Change of the functional group concentration by gas-phase chemical modification with time of exposure to the atmosphere. White is the total functional groups.

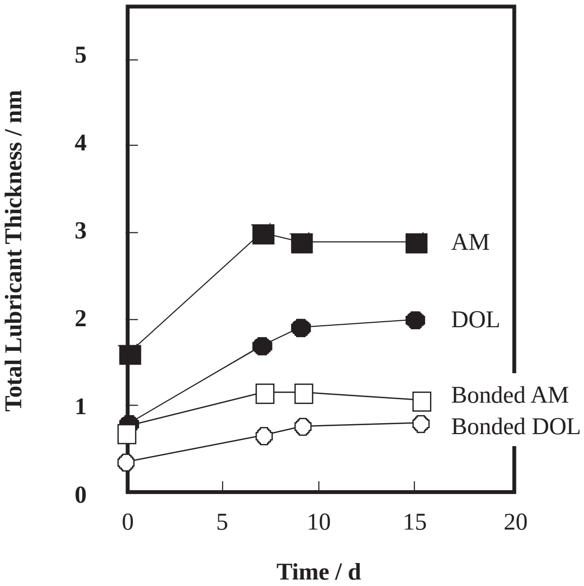


Fig. 9. Lubricant thickness before (black) and after (white) solvent washing. Squares are AM and circles are DOL.

rate, which possibly shows that the oxidation of the carbon surface and the surface polarity can be observed by contact angle measurements. The functional group of the carbon surface was analyzed by XPS, which was preceded by a chemical derivatization. During the initial stage, the amount of hydroxy group was high compared to the other functional groups, but it did not significantly change with time. In comparison, the carbonyl group rapidly increased and became saturated in 5 days, and it became the most abundant functional group. The amount of the carboxyl group was the lowest among these functional groups. The affinity of the surface to the lubricant became stronger upon surface oxidation. The amounts of the adsorbed lubricant increased for the surface oxidized sample and were almost proportional to the number of functional groups.

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