AM 2001 Lubricant Film on Canasite Glass–Ceramic Magnetic Memory Disk

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The AM 2001 fluorocarbon lubricant overlayer on carbon-coated canasite glass–ceramic magnetic memory disks has been characterized by XPS. Lubricant thickness is linear with the concentration of the lubricant in the lubricating solution. For both the carbon-coated and uncoated canasite disks, lubricant thickness can be estimated using either the carbon or oxygen peak intensity. Lubricant thickness can be made reliably and reproducibly on canasite disks while maintaining the same performance characteristics of the lubricating layers as in aluminum disks. The combined properties of superior strength, toughness, microstructure, surface texture, and thinness give canasite significant advantages over competing materials, aluminum, and glass, for use as substrates for hard disks.

Introduction

Fluorcanasite ($Ca_5Na_4K_2Si_{12}O_{30}F_4$), an acicular (needle-shaped) chain silicate glass–ceramic, is used for magnetic memory disks to take advantage of strength, toughness, ruggedness, and microstructures offered by these materials.[1] Canasite provides other potential advantages such as higher reliability at thinner cross sections, higher data densities, high processing temperatures, higher yields, smoother surface texture, and lower costs over current competing substrate materials such as aluminum and glass.

Perfluoropolyether (PFPE) oils have been universally applied as lubricants to magnetic disk surfaces to take advantage of high chemical stability, low vapor pressures and low surface tensions to improve mechanical durability and reduce wear damage to the disk surface. The lubricant thickness has very important consequence to performance. A very thin lubricant layer causes wear damage to the disk surface. Conversely, a thick lubricant layer results in sticking between the head and disk. Lately, decreasing fly height has become an important requirement for the head in computer applications. For these reasons, the control of lubricant thickness to within 2–5 nm is absolutely critical to the performance of magnetic disks.

X-ray photoelectron spectroscopy (XPS or ESCA) is a convenient method of analysis for these lubricating films due to its inherent surface sensitivity and sensitivity to the large chemical shift difference between carbon–hydrogen and carbon–fluorine bonded species. Angle-dependent XPS (ADXPS) which provides nondestructive compositional depth profiling is ideally suited for the determination of the thickness and uniformity of the lubricant overlayer. XPS has been previously used to determine fluorocarbon lubricant thickness on Fe_2O_3/resin winchester disks,[2,3] sputter-carbon-coated aluminum disks,[4] magnetic recording ferrite heads,[5] and analyses of PFPE deposited on electroplated gold substrates.[6] Recently, Mastrangelo et al.[7] used an infrared spectroscopy/grazing angle microscopy combination for the quantification of polyether lube variations on thin-film disks. Viswanathan[8] has shown in a recent report that the thickness of several PFPEs on carbon coated thin-film media can be quantitatively estimated using static secondary ion mass spectrometry (SIMS). However, SIMS requires another technique for standardization. In contrast, XPS, requires no standardization, has a shallow probing depth (<10 nm), is quantitative and provides chemical bonding information. However, all published XPS studies to date involve PFPE oils terminated with trifluoro ($-CF_3$) end groups.

PFPE lubricants terminated by reactive or bondable phenyl-containing end groups such as the AM 2001 are credited with the ability to mitigate the problems of lubricant loss due to spin-off, evaporation, or chemical displacement. This has resulted in the enhanced popularity of these lubricants in the magnetic disk drive industry.[9] Furthermore, with AM 2001, a balance between lubricity and bondability is readily achieved. To the author's knowledge, there are apparently no XPS published studies on PFPE lubrication of glass–ceramic or glass disk substrates. This paper describes the first reported XPS studies of AM 2001 lubricant overlayer on canasite glass–ceramic magnetic memory disk substrate.

Experimental Section

The lubricant was prepared from commercially available FOMBLIN AM 2001 (a trade name of Montedison, Italy, and supplied by Ausimont, Morristown, NJ) oil dissolved in high purity (99.9%) trichlorotrifluoroethane, $C_2Cl_3F_3$ (Freon-TF), solvent. AM 2001 is a linear difunctional perfluoropolyether derivative end-capped with planar chemically reactive piperonyl

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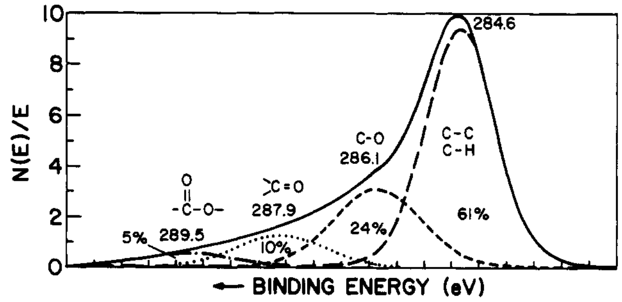

Figure 1. High-resolution C 1s spectrum of unlubed sputter-carbon-coated canasite disk substrate.

groups structurally represented as

$$P\text{-}CF_2\text{-}(O\text{-}CF_2\text{-}CF_2)_m\text{-}(O\text{-}CF_2)_n\text{-}OCF_2\text{-}P$$
$$m/n = 0.9;\ \text{piperonyl},\ P = 3,4\text{-}CH_2O_2{:}C_6H_3\text{-}CH_2\text{-}$$

The lubricant overlayer was prepared by a dip-coating method. The canasite disk samples were dipped vertically into a dilute solution of the lubricant in a bath for 1 min and the solution withdrawn downwards at a constant speed or drain rate using an apparatus constructed in-house. The low boiling point ensured immediate solvent evaporation, leaving behind the lubricant overlayer on the disk surface instantaneously. The desired ranges of lubricant thicknesses were achieved by varying the lubricant solution concentration in the bath and drain rates during application.

XPS analysis was primarily performed on a Perkin-Elmer PHI Model 5500 Multitechnique surface analysis system using Mg Kα radiation (1253.6 eV) from an X-ray source operating at 28 mA, 15 kV (400 W) at a pressure $<1 \times 10^{-8}$ Torr. Some of the data were acquired on a Hewlett-Packard HP 5950A spectrometer using the Al Kα (1486.6 eV) monochromatic radiation. Acquisition time was kept relatively short to prevent volatilization of the lubricant and no rise in pressure was noted during the analysis. Under these conditions the lubricant thicknesses determined with both the PHI and HP instruments were in good agreement within the limits of experimental error (±5 Å). Thickness measurements were also made on lubed surfaces after overnight residence time under high vacuum ($<5 \times 10^{-8}$ Torr). The values obtained indicated essentially no significant lubricant loss (39 vs 35 Å). The PHI instrument was operated with a constant pass energy of 17.9 eV which gave the full width at half-maximum of 0.9 eV for the Ag $3d_{5/2}$ peak over 1 × 3.5 mm analysis area. The binding energy data were charge referenced to a hydrocarbon peak component due to the C–C feature in the disk overcoat. This peak was arbitrarily assigned a value of 284.6 eV. The relative distribution of the observed carbon components were resolved using iterative mixed Gaussian/Lorentzian fit functions.

Results and Discussion

Peak Assignments. The C 1s spectrum of the sputter-carbon-coated disk surface prior to lubrication (Figure 1) showed peaks assigned to various forms of carbon: C–C/C–H (284.6 eV), C–O (286.1 eV), C=O (287.9 eV), and O—C=O (289.5 eV) functional groups. This surface contained 18 atom % oxygen which is well within the range of oxygen concentration (10–20%) normally detected on carbon-overcoated media. This suggests that oxidation had occured on the sputtered carbon surface including some contribution from adsorbed contamination layer. A single oxygen peak centered at 532.3 eV, which probably represents an average energy for both the ether and carbonyl oxygen peaks, was also detected.

Figure 2 is a curve-fitted C 1s spectrum of the pure AM 2001 lubricant smeared on aluminum foil showing seven different functionalities. The peaks at 284.6, 286.2, 288.0, and 290.1 eV were assigned to C—C/C—H, C—O, C=O, and O—C=O funtionalities. A small shoulder at 283.1 eV, probably due to carbidic carbon resulting from thermal effects during XPS analysis, was also observed. These peaks are taken to represent the hydrocarbon (HC) portion in the thickness calculations. The peaks at 291.8, 293.0, and 294.5 eV are assigned to the $\pi \rightarrow \pi^*$ satellite of the phenyl ring in the lubricant piperonyl end group and/or a CFO, C–CF_2–O and O–CF_2–O species, respectively. The latter two peak assignments are consistent with literature values recently reported for bifunctional (type F) perfluoropolyether oils by Mori and Morales.[10] The peaks at 291.8, 293.0, and 294.5 eV represent the fluorocarbon (FC) portion in lubricant thickness determinations. The oxygen spectrum (Figure 3) shows two ether oxygen components: C–O–C (533.3 eV) and F_2C–O–CF_2 (535.7 eV) expected for an AM 2001 lubricant. The F 1s binding energy of 689.0 eV was also measured for the pure lubricant. The XPS atomic composition analysis showed 35.2% carbon, 18.5% oxygen, and 46.3% fluorine. Aluminum signals were not observed, thereby indicating that all species detected are associated with the pure lubricant. This is consistent with the idealized stoichiometry expected for an AM 2001 PFPE oil. Comparison of the lubricated canasite disk spectra with that of the pure lubricant indicated that the surface chemistry of the lubricating layers is identical in both samples. Thus, no extraneous components were added during dilution of the lubricant.

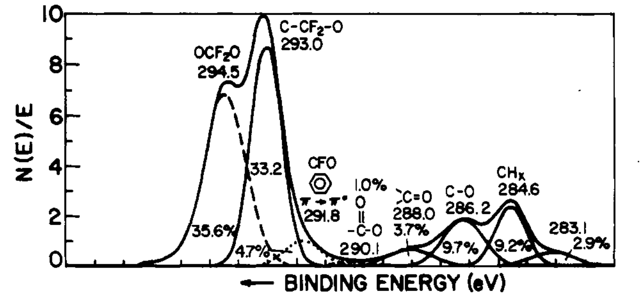

Figure 2. High-resolution curve-fitted C 1s spectrum of pure AM 2001 lubricant showing the relative distribution of chemical functionalities.

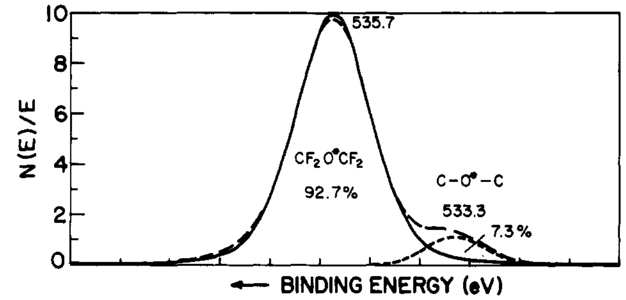

Figure 3. Oxygen 1s spectrum of pure (undiluted) AM 2001 perfluoropolyether lubricant.

Lubricant Thickness Measurements. From the uniform overlayer model proposed by Fadly,[11] film thickness can be related to the angular dependent photoelectron peak intensity by the XPS standard equation for lubricant thickness on hard disks.[12] This equation is

$$d = \lambda \sin \theta \ln(R/R^* + 1)$$

where d is lubricant thickness (in Å), R (FC/HC) is the

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Table I. Binding Energies (eV) for AM 2001 Lubricant on Canasite Magnetic Memory Disk[a]

species	C 1s	O 1s	F 1s
OCF_2O	294.7(13.6)	535.6(66.8)	688.9
CCF_2O	293.2(21.9)	535.6	688.9
$CFO/\pi\rightarrow\pi^*$	291.6(3.6)	535.6	688.9
O—C=O	289.0(4.4)	532.8(33.2)	
>C=O	287.5(6.7)	532.8	
C—O—C	286.1(12.8)	532.8	
C—C/C—H	284.6(37.0)		

[a] In parentheses: relative distribution (%).

Table II. Calculated AM 2001 Lubricant Thickness as a Function of Concentration[a]

concn (wt %)	thickness (Å)	concn (wt %)	thickness (Å)
0.21	23	0.42	52
0.21	23	0.53	56
0.21	26	A-1	32
0.21	25	A-2	35
0.21	33	B-1	30
0.23	36		

[a] A and B indicate commercial lubricated aluminum disk from different vendors.

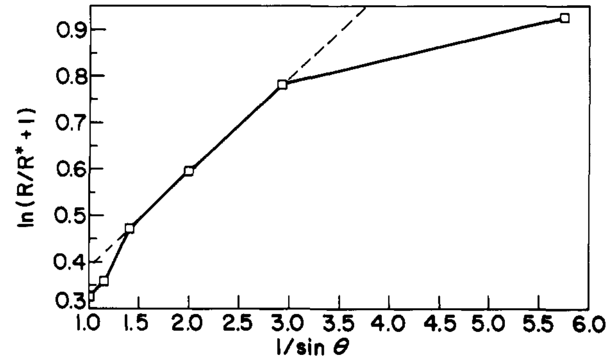

Figure 4. Angle-dependent XPS carbon 1s data for AM 2001 lubricant on sputter-carbon-coated Canasite disk showing deviation from the uniform overlayer model at low photoelectron takeoff angles.

measured lubricant carbon/substrate carbon area ratio at a given angle for a lubricated disk, R^* is the ratio for the carbon peak areas for pure lubricant and unlubed disk substrate, λ is the electron escape depth, and θ is the photoelectron takeoff angle (TOA) measured with respect to the sample surface normal. R^* was experimentally determined to be 0.86 when carbon lubricant/carbon substrate was used and 0.33 when the oxygen lubricant/oxygen substrate was used. A plot of $\ln(R/R^* + 1)$ versus $1/\sin\theta$ gives a slope equal to d/λ. A value of 40 Å for λ was used in the determination. This value was chosen based on a recent literature report which indicated that this was the best value from a comparison of values obtained from a correlation study involving several techniques.[13] Using these values the lubricant thickness is determined from the slope of the graph.

Table I lists the energies and the relative amounts of the component species for a typical AM 2001 lubricated canasite disk. It shows the expected hydro- and fluorocarbon peak components at the right energies for AM 2001, thereby indicating the presence of the lubricant overlayer on the carbon-coated canasite substrate. The high concentrations of C—C/C—H, C—O—C, C=O, and O—C=O species measured for the lubricated canasite disk represent intensity contributions from both the lubricant HC portion and carbon contamination from the unlubed disk. Figure 4 is a graphical plot for a lubricated disk showing that the curve is linear for high TOA angles but deviates at lower angles. This behavior suggests that the XPS lubricant thickness equation is valid only for the angles chosen from the linear portion of the graph. These results are consistent with the observations of Moulder et. al. in their ADXPS study of fluorocarbon lubricants on Winchester disks.[3] The nonideal behavior at lower angle(s) can be attributed to several factors such as nonuniformity in lubricant coverage, surface roughness, or the presence of a contamination layer of surface carbon. In general, lubricant thickness is known in the industry to depend on such variables as how the carbon coating is applied, the way it is applied and handling of the carbon-coated disk prior to lubrication. Other factors which affect thickness include the manner of lubrication, drain rate, and the type of substrate.

Lubricant thickness measurements were also made on Si wafers dip-coated with AM 2001 lubricating solution using the oxygen peak intensity in the graphical overlayer model. R^*, which represents the ratio of the oxygen peak areas for pure AM 2001 lubricant and unlubed Si substrate, was experimentally determined to be 0.33. Assuming $\lambda_{\mathrm{O\,1s}}$ of 40 Å, the thickness of the lubricant layer on the Si substrate was determined by XPS to be ~19 A. Optical ellipsometric measurement on the same sample found that the lubricant layer is 20 ± 1.2 Å thick, thereby corroborating the XPS result. Measurements on bare canasite and microsheet glass slide substrates similarly dip-coated with the same lubricant solution yielded 20- and 18-Å lubricant film thicknesses, respectively. These experiments indicate that reliable lubricant thickness measurements on bare canasite are possible by this method.

The collection and plotting of data generated at various angles are time consuming and undesirable for process control applications. Linder and Mee[1] have shown that a single datum point obtained at a high TOA in the linear part of the curve gives an average lubricant thickness with good precision. From the simplified model developed by the authors, the expression for the thickness of the lubricant layer is

$$d = \lambda \ln(aR + 1)$$

where λ is the electron escape depth (assumed to be 40 Å), a is the carbon atom density in the sputtered carbon overcoat relative to the carbon atom density in the pure AM 2001 fluorocarbon (a = 2.62 estimated from the bulk carbon densities), and R (R = FC/HC) is the measured lubricant carbon/substrate carbon XPS peak area ratio. Table II lists the lubricant thicknesses determined by XPS using the simplified method. An average thickness of 26 Å was obtained from five replicate measurements using this method. This value is in good agreement with values obtained by the graphical method on the same samples. The table also shows that the lubricant thickness increased proportinately with lubricant concentration in the lubricating solution. The simplified method is applicable to lubricant thickness determinations on bare (uncoated) canasite disk substrates using the oxygen XPS peak intensities and the corresponding oxygen atom densities for canasite and the pure AM 2001 lubricant. The data also show that the thicknesses as high as 60 Å desired in the industry can be achieved on a glass-ceramic disk such as canasite.

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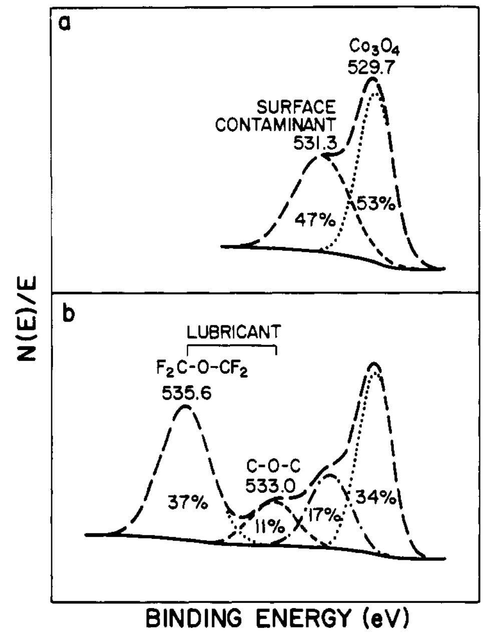

Figure 5. High-resolution O 1s spectral comparison showing surface contamination: (a) oven-baked unlubed carbon-coated canasite disk; (b) oven-baked, then relubed carbon-coated canasite disk.

Studies were undertaken in an attempt to explain the thickness variations observed. In one experiment, a lubed disk was sampled circumferentially at six different random locations and the thicknesses determined agreed to within 5 Å, thereby indicating uniform coverage of the lubricant thin film. The effect of surface contamination on lubricant thickness was also evaluated. A lubed disk was stripped with Freon, baked in an oven at 400 °C/1 h and then relubed with 0.21 wt % solution. The thickness determined was ~10 Å less than the original value. This observation suggests either the presence of significant contamination on the disk surface before lubrication or decreased bondability of the lubricant to the substrate. Figure 5 compares the oxygen spectrum of the baked unlubed disk to that of the relubed disk. It shows the presence of organic oxygen (531.3 eV) contamination on the surface and cobalt oxide (529.7 eV) before and after lubrication. The carbon spectrum (not shown) indicated that the 531.3-eV oxygen peak is bonded to carbon even on the baked unlubed surface. The presence of this oxidized carbon contamination layer will lead to underestimation of film thickness. The presence of the 529.7-eV cobalt oxide oxygen peak, suggests either that the sputtered-carbon overcoat is also removed most likely by the 400 °C process, or much more plausible that the bake caused cobalt migration through the carbon overcoat to the surface of the disk. The data also show that the lubricant was chemically stripped by Freon thereby exposing the Co magnetic layer. It is noteworthy that the cobalt peaks were not detected on the disk surface prior to either the lubrication process or the chemical stripping experiment. This experiment underscores the importance of surface cleanliness before lubrication for reliable and precise lubricant thickness measurements by this method.

For qualification purposes the thickness of commercial carbon coated aluminum disk substrates lubed with AM 2001 from three different sources were determined by XPS using the same algorithms. The C 1s curve-fitted spectra (not shown) of the lubed aluminum disks all show the presence of components expected for an AM 2001 lubricant, except for an additional shoulder peak at 296.5 eV probably due to an $-OCF_3$ moiety. The overall carbon and oxygen spectral patterns obtained were essentially consistent with those obtained for the lubricated canasite disks. The lubricant layer thicknesses obtained from three different samples were all found to be in the 30–35-Å range (Table II). These values are well within the reported thickness range (25–35 Å) of lubricating films on commerical aluminum memory disks.[2,8,14,15] In another experiment, using the oxygen photoelectron signals and the graphical method, a lubricant layer of 30 Å was determined for a sputter-aluminum-coated canasite disk. These experiments demonstrate that the tribological characteristics of the lubricating layer on sputter-carbon- or aluminum-coated canasite glass–ceramic disks should be comparable to those of the commercially available competing aluminum disk substrate material.

Conclusions

It has been shown that the thickness of AM 2001 lubricant layers on carbon-coated canasite magnetic memory disk substrates can be measured reliably by XPS with precision comparable to similarly lubed commercially available aluminum disk substrates. The concentration of the lubricant in the lubricating solution is linear with lubricant thickness and a 0.21 wt % lubricant solution concentration is sufficient to achieve the thickness range of lubricating films for memory disks in the magnetic recording industry. Both surface contamination of the substrate prior to application of the lubricant layer and the inclusion of the intensity of lubricant hydrocarbon portion in the substrate signals have a deflationary effect on the measured thickness for AM 2001. The XPS algorithms for lubricant thickness determinations can be applied to both the carbon coated and uncoated canasite disks using the relative oxygen XPS peak intensity in the overlayer calculations.

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