

Characterization of Micro-Corrosion on Magnetic Recording Disks by ToF-SIMS and AAS

Y. Abe*, M. Shibayama, J. Sasahara and J. Koza
Yokohama Research Center, Mitsubishi Chemical Corporation
1000, Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan
* yosimi@rc.m-kagaku.co.jp

(Received April 9, 1999; accepted April 28, 1999)

In order to qualify thinner carbon overcoats (ranged from 5-11nm) on magnetic recording disks, the Co micro-corrosion from the magnetic layer to the surface after the stressed corrosion test (at 85°C and 80%RH for 4days) has been studied by ToF-SIMS. Analysis of water-extracted Co with AAS was also performed to check the results obtained by ToF-SIMS. Whereas the almost linear correlation of these two measurements can be obtained from the overcoats above 7nm, the Co intensity by ToF-SIMS is much higher than the Co amount by AAS from the overcoat of 5nm. According to the dependency upon the beam energy, it is clearly shown that the relative intensity of Co can be varied by the choice of primary beam energy, and the lower energy (less than 7keV) should be recommended in the case of Co migration analysis of thinly overcoated (below 7nm) disks. Based on the results obtained, we mention that if the beam energy used is too high or the overcoat is too thin, Co from the magnetic layer may be detected through the thin overcoat film by ToF-SIMS.

1. Introduction

Carbon overcoats are widely used for magnetic recording disks as a protective layer against wear and corrosion from interaction at the head-disk interface (HDI). With the requirement of higher data storage capacity, the thin-film media industry has recently focused on developing a thinner overcoat with better wear and corrosion resistivity.

Corrosion of the thin film disks under environmental conditions is believed to be an electrochemical process which requires the presence of water on the surface[1,2]. In order to qualify thinner overcoats, corrosion test stressed under high temperature and high humidity is frequently used to examine whether the migration of cobalt from the magnetic layer to the surface has occurred or not. It is well known that the corrosion stress leads to selective

migration of Co from the magnetic layer which is dependent on disk overcoat composition and structure[5].

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a suitable technique for Co migration analysis because of extremely high surface sensitivity and high lateral resolution[3,4]. In this work, we present the characterization of Co migrated to the surface using ToF-SIMS compared with atomic absorption spectrometry (AAS), which is one of the conventional techniques with good quantification and poor lateral resolution.

2. Experimental

The thin film disks used had a 1.2nm lubricant layer and a different carbon overcoat above a magnetic layer of 25nm CoCrTaPt alloy. Below the magnetic layer, an underlayer of 40nm Cr was

underlying on a NiP-plated Al substrate. The lubricants were Fomblin Z-DOL, which has the backbone of perfluoropolyethers (PFPEs) with hydroxyl end groups. The lubricant thickness was measured by Fourier-transform infrared spectroscopy (FTIR)[12] and/or X-ray photoelectron spectroscopy (XPS)[13]. The overcoats were hydrogenated carbon prepared by chemical vapor deposition (CVD) or DC magnetron sputter, and their thickness was ranged from 5nm to 11nm (tabulated in table 1). Thickness of overcoats was estimated by electron probe micro-analyzer (EPMA) calibrated by transmission electron microscope (TEM). Samples of B-E or F-G with the same preparation and the same thickness were deposited under various conditions, respectively, which probably led to the different carbon density or hydrogen content on the analogy of other measurements by hydrogen forward scattering spectrometry - Rutherford back scattering spectrometry (HFS-RBS).

Table 1. Carbon overcoats of tested samples.

Sample name	Preparation	Thickness (nm)
A ^{*1}	CVD	5
B ^{*1}	CVD	7.5
C ^{*1}	CVD	7.5
D ^{*1}	CVD	7.5
E ^{*1}	CVD	7.5
F ^{*2}	Sputter	11
G ^{*2}	Sputter	11

^{*1} Carbon density of CVD samples may be varied as follows: A and B > C > D > E.

^{*2} Hydrogen content of sputtered samples may be varied as follows: F > G.

The disks then subjected to high temperature (85°C) and high humidity (80%RH) in a commercial humidity

chamber for 4 days. The ramp up rate of the temperature and humidity was kept minimum to avoid possible water condensation on the disk surface.

ToF-SIMS was performed in a PHI TRIFT II system with a pulsed Ga liquid metal ion gun operating at various energies of 2, 7, 12 and 22keV. The beam current was set to 600pA DC and the beam raster size was 40um x 40um at the acquisition of spectra. In this system, the sample holder was biased with a 3kV positive voltage at the acquisition of positive ions. Positive ToF-SIMS spectra and images were obtained from the disks after the stressed corrosion test (at 85°C and 80%RH for 4 days).

AAS analysis of Co cation dissolved in water was also performed to check the results obtained by ToF-SIMS. For the AAS measurements, the tested disks were steeped in water for 30 minutes at room temperature in order to extract the corrosion products on the surface. Before the stressed corrosion test, Co was not detected from all the samples by AAS.

3. Results and Discussion

On the ToF-SIMS spectra obtained by 7keV beam, the C_xF_y type of fragments originating from the backbone of lubricant are dominated as previously reported[7-9], and Co peak is additionally observed at 58.93 atomic mass unit (amu) from the sample A, D, E, F and G. Figure 1 shows the relationship between the ratio of Co/CF₂ in intensity by ToF-SIMS and the Co amount detected by AAS. In the AAS measurements, the limit of quantification for Co was estimated at 0.005 ug/piece, which corresponded to 4 x 10¹¹ atoms/cm². On

the ToF-SIMS spectra, intensity over 50 counts was regarded as a peak after the data acquisition for 3 minutes. At this conditions total primary ion dose was estimated at 8×10^{12} ions/cm², several times higher than the generally accepted static limit[10], in order to ensure whether the Co peak was present or not on the spectrum.

The almost linear correlation of these two measurements can be observed except sample A (noticed by an arrow in fig. 1), which has the thinnest overcoat of 5nm. In the case of sample A, the Co intensity obtained by ToF-SIMS is much higher than AAS.

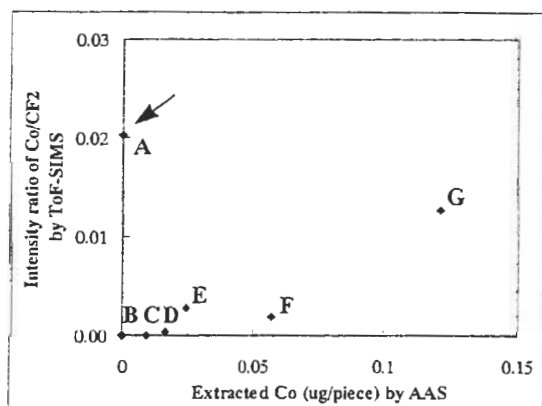
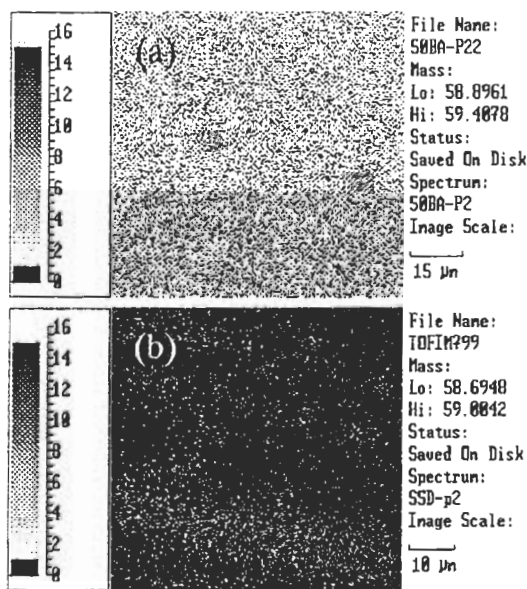


Figure 1. Relationship between ToF-SIMS and AAS.

Some different behavior is also shown by the ToF-SIMS imaging. Figure 2 (a) and (b) show the Co distribution from the sample A and G, respectively, obtained by 22keV beam, which has the advantage of lateral resolution less than 1um. The Co distribution of sample G correlates with the texture lines in agreement with previous works[5,6], while an uniform coverage is only observed from the sample A. Here we point out that there is no sign of Co corrosion on the sample

A from the ToF-SIMS imaging.

To understand the difference between the sample A and others, we examined the dependency of the Co intensity upon the primary beam energy.



Comments: Co Image

Figure 2. Positive ToF-SIMS images of Co from the sample of (a) A and (b) G, respectively, obtained by 22keV beam. The beam raster size was (a) 80um x 80um or (b) 60um x 60um.

Figure 3 shows the positive ToF-SIMS spectra obtained by 2, 7, 12 and 22keV beam, respectively, from the sample A. An incidence angle becomes near normal as the primary beam energy increases in this system (for example, 75° for 2keV, 45° for 7keV, 41° for 12keV, and 38° for 22keV[11]). The mass resolution of $m/\Delta m$ for Co was over 7000 at 2, 7, 12keV or about 3000 at 22keV. Figure 4 shows the normalized intensity of CF, C2F4 and Co (shown in fig. 3) against the beam energy in the case of sample A. All intensities shown in fig. 4 are normalized to the CF2 intensity

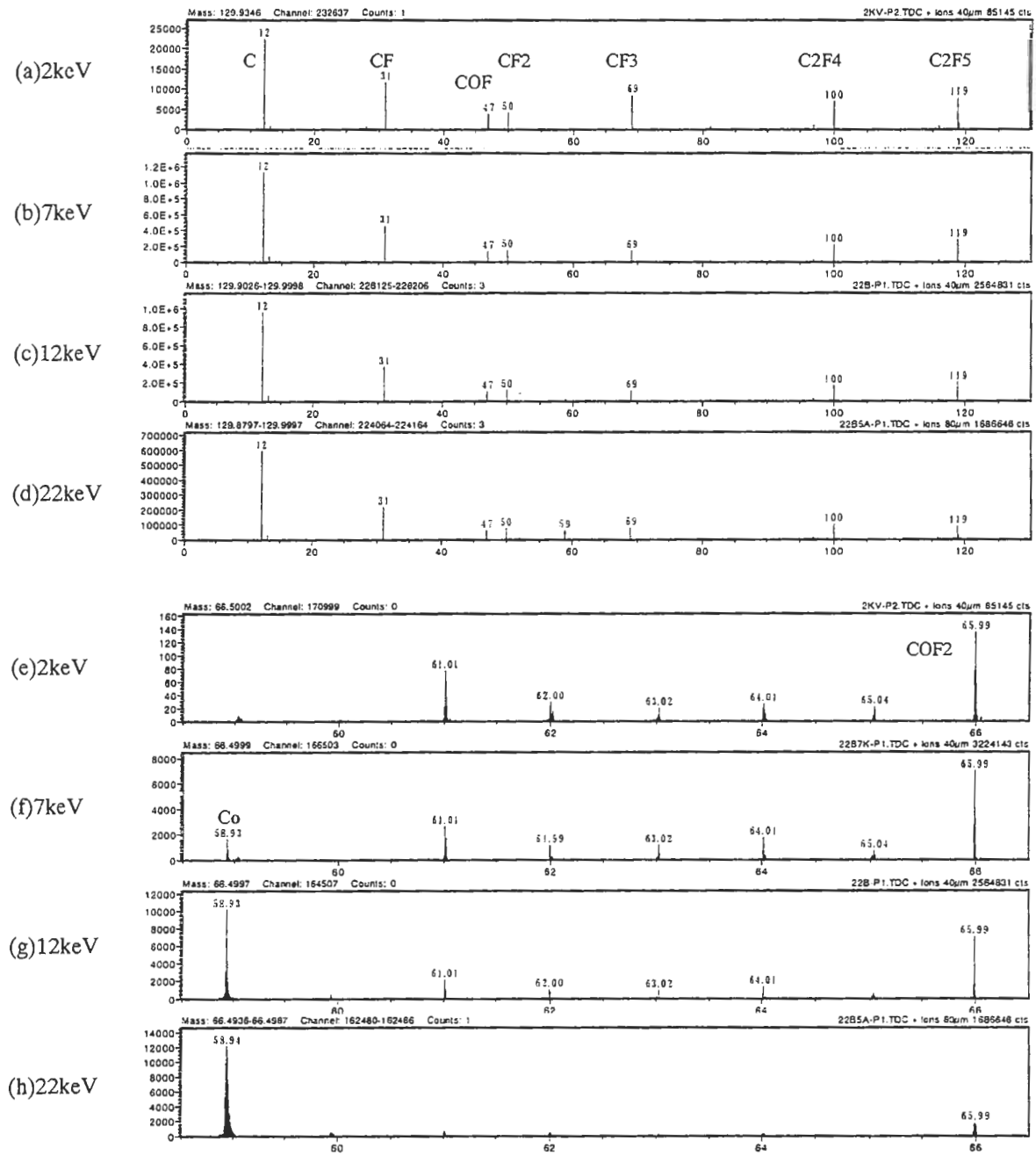


Figure 3. Positive ToF-SIMS spectra from the sample A by (a)(e) 2keV, (b)(f) 7keV, (c)(g) 12keV and (d)(h) 22keV beam, respectively.

of each spectrum. Whereas the relative intensities of CF and C2F4, originating from the lubricant, are almost independent on primary beam energy in agreement with previous work[11], the relative intensity of Co can be varied by the choice of primary beam energy.

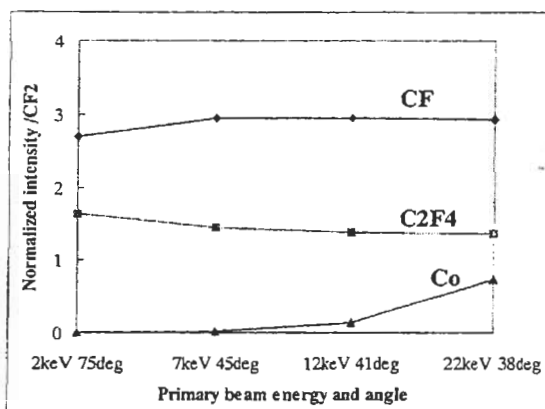


Figure 4. Changes in intensity normalized to the CF2 peak as a function of primary beam energy and angle of incidence.

Based on the results obtained, we can conclude that the relative intensity of Co is strongly dependent on the primary beam energy and the lower energy should be recommended in the case of Co migration analysis of thinly overcoated (probably below 7nm) disks. If the beam energy used is too high or the overcoat tested is too thin, Co from the magnetic layer may be detected through the thin overcoat film and some misjudgments may be extracted in the qualification of thin overcoats.

Acknowledgement

The authors would like to thank M. Tozu of ULVAC-PHI, Inc. for precisely operating the ToF-SIMS system.

References

[1] V. Novotny and N. Staud, *J.*

Electrochem. Soc., vol. **135**, 2931 (1988).
 [2] C. C. Wang, R. W. J. Chia, J. K. Lee and W. T. Tang, *J. Vac. Sci. Technol. A*, vol. **16**, 1745 (1998).
 [3] A. Benninghoven, *Surf. Sci.*, vol. **299/300**, 246 (1994).
 [4] A. Benninghoven, *Angew. Chem. Int. Ed. Engl.*, vol. **33**, 1023 (1994).
 [5] L. J. Huang, Y. Hung and S. Chang, *IEEE Trans. Magn.*, vol. **33**, 3154 (1997).
 [6] T. J. Schuerlein, C. A. Evans and P. M. Lindley, *Proc. SIMS XI*, 615 (Wiley 1998).
 [7] J. G. Newman and K. V. Viswanathan, *J. Vac. Sci. Technol. A*, vol. **8**, 2388 (1990).
 [8] P. H. Kasai and A. M. Spool, *J. Phys. Chem. B*, vol. **102**, 7331 (1998).
 [9] 阿部芳巳, 柴山雅子, 松尾武士, 第18回表面科学講演大会要旨集, 87 (1998).
 [10] D. Briggs and M. J. Hearn, *Vacuum*, vol. **36**, 1005 (1986).
 [11] T. Hoshi, M. Tozu, R. Oiwa and L. Zhanping, *Appl. Surf. Sci.* vol. **121/122**, 146 (1997).
 [12] V. J. Novotny, I. Hussla, J.-M. Turllet and M. Philpott, *J. Chem. Phys.*, vol. **90**, 5861 (1989).
 [13] M. F. Toney and C. M. Mate, *IEEE Trans. Magn.*, vol. **34**, 1774 (1998).

査読者との質疑応答

査読者：塚本和芳（松下テクノロジー）
 柳内克昭（TDK）

塚本：

質問1：AASですが、30分の水抽出で腐食したCoが十分回収できているか否かの議論が必要ですが、確かめられていますか？

著者：抽出時間については十分な予備検討を実施し、30分で十分回収できている

と考えます。また、液中AFM観察により、腐食生成物が水中で直ちに消失（溶解）することも確認しています。

質問2：CF2でTOF-SIMS強度を規格化していますが、何故CF2で規格化しているかの理由を教えてください。

著者：二次イオンの検出強度は、試料の潤滑剤膜厚や測定条件、装置コンディションなどに依存して変化します。相対的な強度変化の傾向を見る目的で、潤滑剤由来の主要フラグメントの中からCF2を選択し、規格化した相対強度として議論を進めました。ここで、規格化の分母としてCF2にこだわる必然性は特にありません。

質問3：初期値として、as-received (stressed corrosion testをしていない)試料でのデータが必要ですし、高加速エネルギーによるescape depthの増加によるCoの検出の問題は本来Coが全く検出されないはずのas-receivedの試料ですべきではないでしょうか？

著者：as-received試料の初期値としては、AASでは全試料でCo非検出(0.005ug/枚以下)です。このため、ToF-SIMS測定は実施していません。これを本文に書き加えました。また、ビーム条件を展開した実験の試料選定に関しては、試料Aでは腐食加速試験後もAASでCoが全く検出されないことから、実験目的に支障ないと判断して試料に用いました。as-received試料を用いても傾向が変わらないことは、別の実験で確認しています。

質問4：p.4左側部の下から7行目の文章で、何故図2から試料Aでcorrosionが無いといえるのでしょうか？

著者：腐食が発生した場合には、Co酸化物または水酸化物などの表面析出物が点在する様子がAFM観察などにより確認できます。この場合、析出物の位置に対応してCoが分布するようなCoイオン像が得られますが、試料AのCoイオン像には

こうしたCoの偏在が全く認められません。

質問5：この実験に用いたような試料は表面の凹凸が存在し、かつ各層の膜厚もマイクロに観察した場合、かなりばらつきがあるものだと考えられますが如何でしょうか？その意味で図1で試料Aは部分的に下地が見えているだけではないでしょうか？

著者：ご指摘の通り、表面凹凸や膜厚のばらつきは存在しますが、もし部分的に下地が見えているとすれば、AASでCoが検出されない実験事実を説明できません。下地が覗いていたとすれば、多大な量のCoがAAS検出されます。

質問6：p.6左側部の図4ですが、一次イオンエネルギーによりatomic mixingを受け下地のCoが検出されるといっておられると思いますが、それならば磁気層の他の構成元素、例えばCrも検出されるはずですがどうでしょうか？感度は悪いと思いますがTa, Ptはどうでしょうか？逆に、構成元素の依存性が明確になれば物理的にもかなり面白いとおもいますが。

著者：ご考察の通り、磁性膜を構成するCo, Cr, Ta, Ptのうち、Coが多量に検出されたビーム条件ではCrやTaも同時に検出されており（Crは7keV以上、Taは12keV以上で検出）、本文に記載したCoの強度傾向と合致した変化を示しています（下図）。磁性膜はCo含有量が70at%を超えるCoベース合金ですので、本文では代表例として、Coの挙動を記載しています。

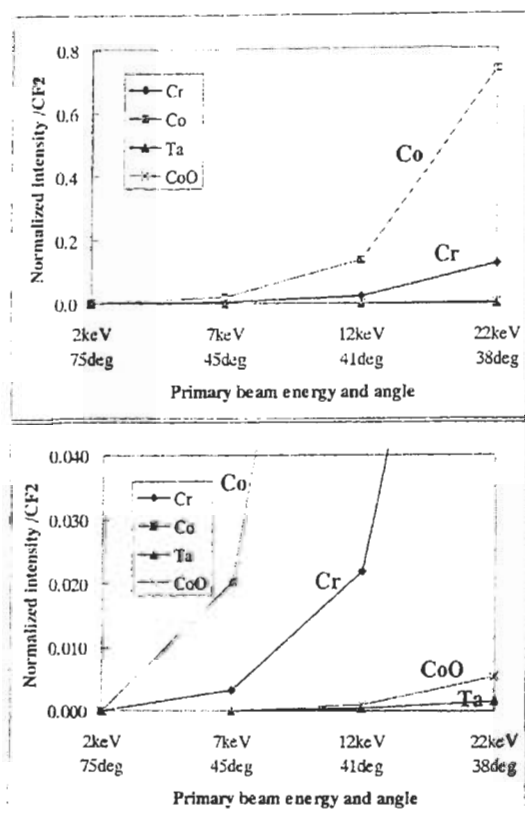


Figure 5. Changes in intensity normalized to the CF2 peak as a function of primary beam energy and angle of incidence.

質問7：図4で、横軸に単なる加速電圧をとっていますが、p.3に折角一次イオン入射角の一次イオンエネルギー依存性を述べているのですから、 $E \cos \theta$ で表記した方がもっと物理的な意味合いを持つのではないのでしょうか？

著者：ご指摘を考慮し、引用文献[11]に倣ってエネルギーと入射角を横軸に併記しました。

質問8：図4は試料Aで測定されていますが、本来ならば未処理の試料Aで行うべきではないのでしょうか？

著者：質問3に回答した通りです。

柳内：

質問1：Table 1のsample B~E及びFとGの違いが一見してわかりません。水素量の大小関係、密度の大小などを示す項目を追加した方がよいと思います。

著者：試料に用いたC保護膜は膜厚範囲が5-11nmの薄膜であり、RBS-HFSの実測は困難な状況です。同じ成膜条件で成膜した厚膜でのRBS-HFSデータから導いたおおよかな類推を一部、表1に書き加えました。

質問2：同様にFigure1のA以外がどの点に対応するのかが示されていません。カーボン膜質との関係も明確になり、説得力が増すと思います。

著者：ご指摘の通り、図1に試料名を書き加えました。

質問3：corrosion test後に表面に析出したCoは酸化物あるいは水酸化物となっていると考えられます。ToF-SIMSでCoOやCo(OH)2などに対応するMass spectrumは得られなかったのでしょうか。加速電圧を上げることでCoO、Co(OH)2が還元されて、Coとして検出されていると考えられないのでしょうか。Coの上昇と伴って65.99のCOF2の比率が減少している点もOが脱離したためと思われるのですが、どのように考察されますか。

著者：スペクトル上で、Co(OH)2は確認できませんが、CoOに対応するピークは検出されています(12keV以上のビーム条件で)。塚本氏の質問6への回答として追加した図5にCoOの強度傾向も示しました。ただし、強度はCoピークの1%未満に過ぎません。酸化物であっても、Co+イオンとして検出される場合が支配的ですので、ビーム条件の展開実験ではCoピーク強度を議論しています。

「Coの上昇と伴って65.99のCOF2の比率が減少...」というコメントは、図3から導かれたものと思いますが、図3では最大ピーク強度に合わせて強度軸のスケールを変えています。図4に示した通り、潤滑剤のフラグメントパターンには大きな変化が認められていません。