

Improvement of Durability and Corrosion Resistance of Metal Evaporated Tape with Chemically Deposited SiO_x Overcoat

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Abstract—To improve reliability of metal evaporated tape (ME tape), SiO_x overcoat was investigated. Durability of ME tape overcoated with SiO_x was greatly improved by lubricating with C₁₈H₃₇OP(H)(O)OH (mono octadecyl phosphite: MOP), which showed more than 10 hours life time in still mode durability test (relative speed of head to media:11.3m/s). Since MOP was solid at room temperature, adhesion did not occur and friction force during the test reduced by 25% compared with perfluoropolyether liquid lubricant. Corrosion of ME tape was prevented by SiO_x overcoat prepared by plasma enhanced chemical vapor deposition (PECVD). Water transmission rate of PECVD-SiO_x was one tenth of physically deposited SiO_x, which well suppressed surface corrosion of ME tape in the atmosphere of 60 °C 90%R.H. and of 4 ppm SO₂ (40°C 80%R.H.).

1. INTRODUCTION

Obliquely metal evaporated tape (ME tape) shows excellent read/write characteristics using ring type head, therefore, it is a strong candidate of media for high density digital recording system[1],[2]. In the system, relative speed of head to media becomes more than 10 m/s[3], which is about three times faster than that of Hi8 VTR system now in use. In such a case, even perfluoropolyether (PFPE) liquid lubricants degrade when ME tape is directly lubricated with PFPE. In addition, non-magnetic CoO thin layer which exists at the surface of ME tape is chemically unstable. Therefore, chemically inert and stable overcoat is necessary to improve ME tape reliability.

Carbon overcoat is widely used in hard disk media because it has self-lubricity as well as good chemical stability. Recently, diamond like carbon (DLC) overcoat has been studied for ME tape[4],[5], however, its deposition rate is low and it is difficult to deposit on large area. Silicon oxide (SiO_x), which is another candidate of the overcoat, can be deposited with higher deposition rate and is superior to DLC overcoat in manufacturability. In this paper, we report on improvement of durability and corrosion resistance of ME tape with a SiO_x overcoat.

2. EXPERIMENTAL

To investigate the chemical properties of ME tape surface, non-magnetic CoO thin film was prepared by sputtering. Non-magnetic NiO thin film was also prepared for comparison. CoO magnetic thin film (ME tape) of 0.13 μm thick was obliquely evaporated (incident angle:90° ~55°) on 10 μm thick polyethylene terephthalate (PET) base film in an oxygen atmosphere using a continuous roll coater apparatus. SiO_x overcoats were deposited on the ME tape by physical vapor deposition (PVD:vacuum deposition and sputtering) and by plasma enhanced chemical vapor deposition (PECVD). Durability of the tapes was tested under two conditions summarized in Table 1. Corrosion resistance was examined

Table 1
Conditions of Durability Tests

Test mode	Load	Tape Tension	Rubbing Speed	Rubbing Width	Atmosphere
A:Sliding	5 gf	-	0.33m/s	0.02m	25°C 40%R.H.
B:Still	-	12.5gf/cm	11.3m/s	0.08m	25°C 40%R.H.

under the atmosphere of 60 °C 90%R.H. and of 4 ppm SO₂ (40°C 80%R.H.). Water transmission rate through SiO_x overcoats on 10 μm thick of PET film was also measured in the atmosphere of 40°C 90%R.H.

3. RESULTS and DISCUSSION

Chemical Properties of Non-magnetic CoO Film

Non-magnetic CoO layer exists at the surface of ME tape. In this section, chemical properties of the film are discussed in comparison with those of NiO thin film. Fig. 1 shows O1s x-ray photoelectron spectroscopy (XPS) spectra of sputtered CoO and NiO thin films after exposure to air at 25 °C 40 % R.H. for 4 and 10 days. Tables 2 and 3 show O1s peak separation in each film. In CoO thin film, O²⁻ component is dominant just after film preparation, however, OH⁻ component becomes dominant with increasing exposure time. On the other hand, O²⁻ component is still dominant in NiO thin film after 10 days exposure. These results indicate that surface of CoO easily chemisorbs water to form Co(OH)₂. The Co(OH)₂ has layered structure as shown in Fig.2, and hydroxyl layers are weakly hydrogen-bonded to each other. Therefore, durability of non-magnetic CoO thin film covered with Co(OH)₂ is to be weak.

In the digital recording system, the relative speed of head to media becomes more than 10 m/s[3], which will cause extremely high pressure and flash temperature during the motion[6]. Changes of PFPE liquid lubricant were studied when it was rubbed directly on the non-magnetic CoO thin film

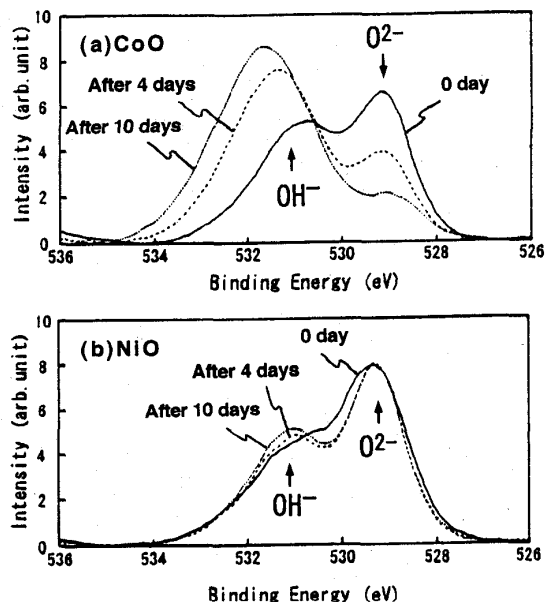


Fig.1. Changes in O1s XPS spectra of (a) non-magnetic CoO thin film and (b) non-magnetic NiO thin film exposed to air at 25°C 40% R.H.

Table 2
Peak separation in O1s of CoO thin film

Exposure time	CoO	Co(OH) ₂	Organic	Co(OH) ₂ /CoO
0 day	45	36	19	0.80
4 days	23	25	52	1.09
10 days	10	21	69	2.10

Table 3
Peak separation in O1s of NiO thin film

Exposure time	NiO	Ni(OH) ₂	Organic	Ni(OH) ₂ /NiO
0 day	55	25	20	0.45
4 days	50	29	21	0.58
10 days	48	31	21	0.65

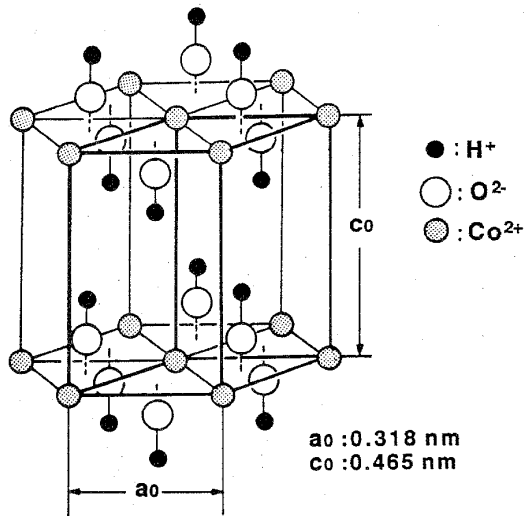


Fig.2. Crystal structure of Co(OH)₂.

by using sliding mode durability test (test A in Table 1). Fig. 3 shows F1s and Co2p XPS spectra of the steel ball surface after 1000 cycles of the sliding test (lubricant: Fomblin-Z-DOL). The main peak of F1s shifted to lower binding energy of 685 eV and that of Co2p shifted to higher binding energy of 783 eV, which indicates that CoF₂ was formed after the sliding test. Furthermore, signal attributed to -CF₂- bond in F1s spectra almost disappeared after the test. Same test was performed on non-magnetic NiO thin film, however, the formation of NiF₂ was scarcely observed. These results implies that PFPE oil decomposes under extremely high pressure by catalysis of Co oxide[7] or Co hydroxide. Therefore, chemically inert and stable overcoat is necessary on ME tape when PFPE liquid lubricants are used.

Silicon Oxide Overcoat for ME Tape

As the overcoat, SiOx thin film was selected because it is chemically stable and is suitable for mass-production (Table 4). Since SiOx thin film has no self-lubricity, lubricant which strongly adsorbs on the surface is necessary. We found that friction and wear were reduced significantly by lubrication with C₁₈H₃₇OP(H)(O)OH (mono octadecyl phosphite:MOP). In the sliding test, SiOx(10nm)/ME tape lubricated with MOP showed friction coefficient of 0.18 and durability of more than 10⁴ cycles, which is superior to the lubrication with Fomblin-Z-DOL. The MOP showed excellent

Table 4
Productivity of Overcoats

Overcoat	Deposition Width	Webbing Speed
DLC	~0.25 m	~10 m/min.
SiOx	0.5~1.5 m	50~100 m/min.

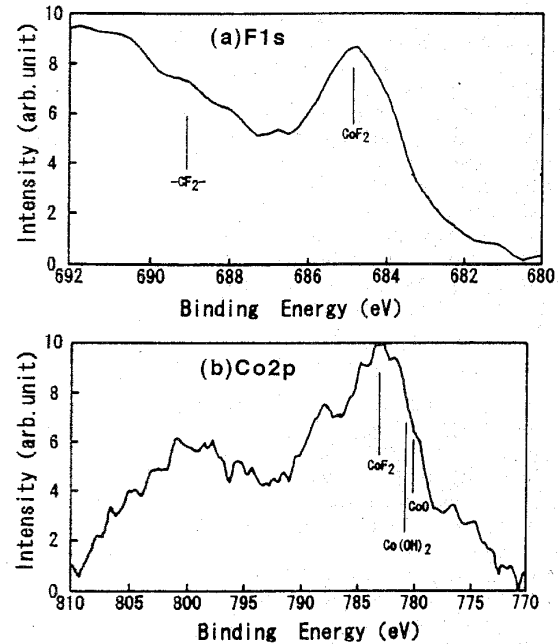


Fig.3. XPS spectra of (a) F1s and (b) Co2p on steel ball surface after 1000 cycles of sliding test. Sliding surface was non-magnetic CoO film lubricated with Fomblin-Z-DOL.

lubricity even after the removal of physisorbed molecules by ultrasonic washing, which indicates that MOP strongly adsorbs on the SiOx surface. In still mode durability test (test B in Table 1), MOP/SiOx(10nm)/ME tape showed more than 10 hours life time. During the test, friction force between cylinder and MOP/SiOx/ME tape was smaller by 25% than that in Fomblin-Z-DOL/SiOx/ME tape. Since MOP is solid at room temperature, adhesion between tape and cylinder did not occur even when a very smooth surface was used as a base film.

The origin of the excellent lubricity of MOP was investigated by angle resolved XPS (AR-XPS) technique. To clear the adsorption state of MOP at the surface, physisorbed MOP molecules were removed by ultrasonic washing in n-hexane. The average adsorption thickness of MOP was estimated to 2.1 nm and this value is close to chain length of C₁₈H₃₇, which suggests that MOP adsorbs on SiOx surface in mono-layer state. Fig. 4 shows AR-XPS spectra of MOP/SiOx after washing. Intensity of P2p decreased with increasing detection angle θ (θ is angle from normal direction of the film). Water contact angle on SiOx increased from 14° to 70° with MOP. These results indicate that MOP molecules adsorb on SiOx with orientating their P atom to the surface, and that C₁₈H₃₇ chains act as boundary lubricant.

The other important role of the overcoat is to prevent corrosion of ME tape. Table 5 shows changes of surface Co concentration (in at.%) of ME tapes overcoated with 20 nm

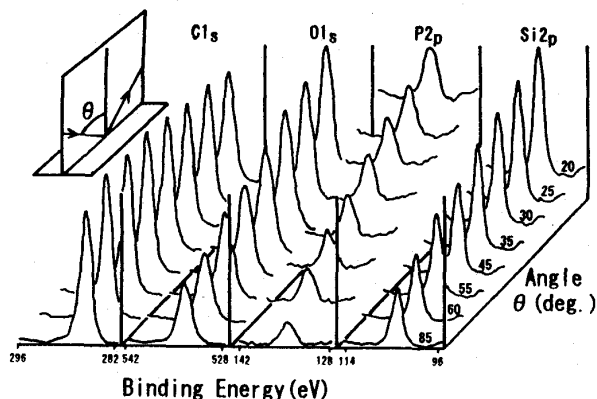


Fig.4. AR-XPS spectra of SiOx surface lubricated with MOP (after washing).

thick of SiOx in the atmosphere of 60 °C 90%R.H. It is clear that PECVD-SiOx overcoat well suppressed Co migration compared with PVD-SiOx overcoats. Fig. 5 shows surface scanning electron micrograph (SEM) of ME tape exposed to the atmosphere of 4 ppm SO₂ (40°C 80%R.H.) for 30 min. ME tape overcoated with sputtered SiO₂ corroded and the surface was perfectly covered with CoSO₄ and CoS, while the corrosion was fairly suppressed by PECVD-SiOx overcoat. In the PECVD method, atoms and small molecules should accumulate from every direction to make a dense film. On the other hand, in the PVD method, clusters accumulated from one direction without enough diffusion, which resulted in a loose film with many vacancies. Therefore, coverage of SiOx overcoat on ME tape should be higher when it is deposited by PECVD method. Table 6 shows water transmission rate through 10 μm thick of PET films. The rate of PECVD-SiOx coated PET is one tenth of PVD-SiOx coated ones, which well supports our discussion mentioned above.

Table 5
Changes of Surface Co Concentration

Overcoat	1 day	3 days	7 days
PECVD-SiOx	0.30	0.31	0.32
Sputtered SiO ₂	0.65	1.07	1.11
Vacuum deposited SiOx	0.51	0.99	1.21

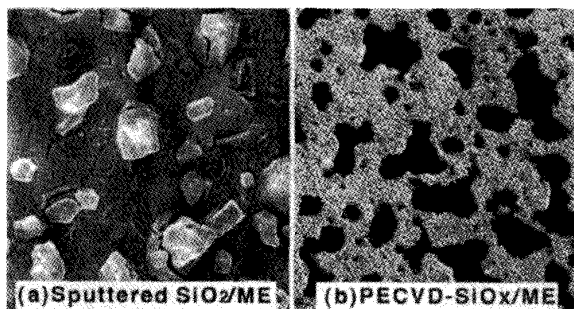


Fig.5. Scanning electron micrographs of ME tape surface after exposure to the atmosphere of 4 ppm SO₂ for 30 min. (a) sputtered SiO₂/ME tape, (b) PECVD-SiOx/ME tape (×3000).

Table 6
Water Transmission Rate of PET Film

Overcoat	Water Transmission Rate
Non	56.4 g/m ² /day
PECVD-SiOx	2.5 g/m ² /day
Sputtered SiO ₂	25.3 g/m ² /day
Vacuum Deposited SiOx	27.8 g/m ² /day

4. CONCLUSIONS

Durability of ME tape overcoated with SiOx was greatly improved by lubrication with mono octadecyl phosphite (MOP). MOP molecules strongly adsorb on the SiOx surface with orientating their P atoms to the surface and straight hydrocarbon chains acted as boundary lubricant. Chemically deposited SiOx overcoat showed much lower water transmission rate compared with physically deposited ones, which also suppresses surface corrosion of ME tape.

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