Plasma Polymerized Protective Films for Plated Magnetic Disks

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Synopsis

Plasma polymerized protective films (PPP films) for magnetic disks have been investigated in order to improve weak durability of plated disk media to head friction and clash. The thickness heterogeneity of PPP films within 5% was realized around the all surface of 140 mm$^\phi$ model substrates, determining the best discharge condition and apparatus geometry, which did not exert an aggravating influence upon head floating. The friction coefficients of PPP films to a ferrite slider of $0.3 \sim 0.4$ were obtained in the thickness of above near 1500 Å, although PPP films are composed of hydrocarbon or fluorocarbon. As the results of contact start/stop cycle tests by a floating head, plasma polymerized toluene-2,4-diisocyanate films show good abrasive durability because of its superior adhesiveness to metal substrates, and PPP films in small thickness near 1000 Å give good protective films. The result of read/write tests indicated that the magnetic deterioration and instability of plated disk media did not occur by the process of plasma polymerization.

INTRODUCTION

Plasma polymerization[1] is a superior technique for forming thin polymer films from almost all organic vapors. Plasma polymerized films are, in generally, highly crosslinked, insoluble, and chemically inert as well as thermally stable. Many applications such as reverse osmosis membranes, insulating layers, and protective coatings have been investigated with much industrial interest. Uniform and pinhole-free films on flat metal substrates are expected from plasma polymerization because of a relatively small-mean free path of monomer gas in the discharge. The protective coatings for juice cans and steel panels have been, therefore, explored.[2,3]

On the other hand, accompanying the development of more large and high speed computers, magnetic disks with more large memory capacity and greater data transfer speed are required as external file memories. Chemically plated Ni—Co—P films have excellent properties for disk medium, e.g., the recording densities of 800–1050 bit/mm have been reported.[4] However, very thin Ni–Co–P films which are called for to achieve the high recording density have weak durability for the friction and clash of heads. Some protective films for Ni–Co–P media such as plated rhodium and chromium,[4] sputtering SiO_2[4] and spin-coated overcoat[5] have been investigated.

The excellent frictional and lubricative properties should be required fundamentally for protective films of plated disks. The protective films must have the thickness as thin as possible, because the recording density decreases according to the increase of the distance between the magnetic medium surfaces and heads, and the thickness of protective films is added to the distance. Be-

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sides, protective films must have the thickness homogeneity as high as possible, because the head floats to follow the film surface at constantly small height.

In this paper, the application of the plasma polymerization technique to apply the protective films of plated disks has been studied. Some properties of the protective film are examined and discussed.

EXPERIMENTAL

The sectional view of plated disks, in which the plasma polymerized protective film (PPP film) is applied in the current work, is shown in Figure 1. In practice, when a disk is not driven, a head is in contact with the disk surface. Immediately after the disk is started to drive, the head floats at constant height from the disk surface. This type is called the floating head.

Substrates

The doughnut-shaped substrates as a disk model were shaped about 2 mm in thickness, 140 mm in outside diameter, and 50 mm in inside diameter. Chemically plated Ni–P films in thickness of 100 μm on aluminum alloy disks were finished by mechanical polishing to the roughness of $R_{max} = 0.02$ μm. Finished Ni–P surface gave Vickers Hardness (H_v) of 550. The substrates were defated sufficiently by dipping and electrolysis in alkali solutions before use.

Monomer Preparations

Monomers used for PPP film which were selected on refering to bulk polymer properties were toluene-2,4-diisocyanate (TCy), α-pyrrolidone (α-Pyr), tetra-fluoroethylene (4FE), and hexafluoropropylene (6FP). The commercially available monomers of TCy, α-Pyr, and 6FP were used without further purification. 4FE monomer was prepared by debromination from 1,2-dibromo-tetrafluoroethane in the same manner as dechlorination from 1,2-dichlorotet-rafluoroethane.[6]

Plasma Polymerization

The apparatus used was an ordinary capacity coupled discharge system, consisting of a glass chamber, flat-bed electrodes, antielectrodes, a monomer introduction line, a vacuum line, and a discharge power supply, as shown in Figure 2.
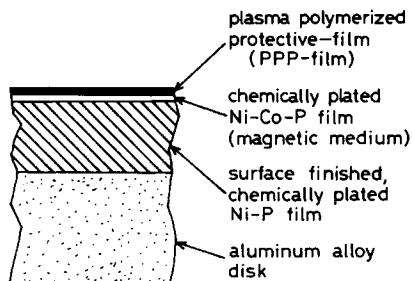

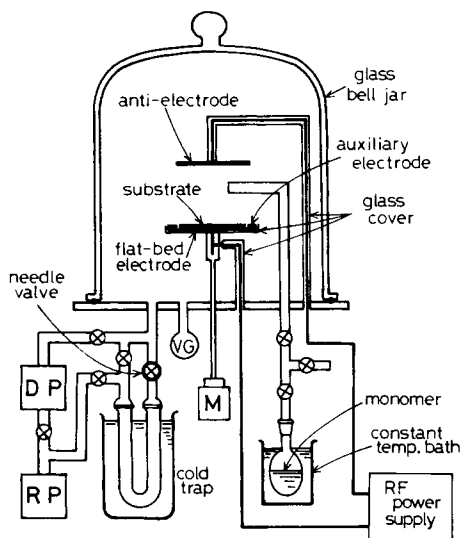Fig. 1. The sectional view of plated disks studied in current work.

Fig. 2. Schematic of apparatus for plasma polymerized protective films.

The large glass chamber (400 mm in diameter, 500 mm in height) auxiliary electrodes attached to the substrate edge, and the rotation of the substrate were used in order to obtain highly homogeneous thickness films over all surface of the substrate.

The substrate was set on the flat-bed electrode with the auxiliary electrodes, and the chamber was evacuated to the pressure of 10^{-4} Torr or less; then vaporized monomer was introduced in the chamber. The monomer pressure was adjusted by a needle valve maintaining the monomer at a given temperature. In this state, constant monomer flow rates were realized. Radio frequency power for discharge was supplied by Model UV-500 (Cho-onpa Kogyo Co., Ltd.) operating at 800 kHz. A 13.56-MHz power supply by VDS-61 (Nippon Electric Company Ltd.) was only used for 4FE discharge without an impedance matching network.

The deposited PPP-film thicknesses were determined by measuring step heights with Dek Tak (Sloan Instruments Corp.)

The Friction Tests of PPP Films

Friction coefficients of PPP-films were measured by the apparatus shown in Figure 3.

The slider which contacted the PPP film was made of ferrite, as were the practical heads. The top of the slider was shaped into the hemisphere (5 mm in diameter) and it was finished to the roughness of R_{max} = 0.02 μm by mechanical polishing. The slider was held to an arm through two pairs of parallel leaf springs A and B. The springs A and B were placed orthogonally. The slider was, therefore, always in contact with the PPP film surface in the same attitude. As the arm is lowered, load from the slider to PPP films was applied by the flexure of spring A. The magnitude of load was detected by strain gages which were attached to the most flexible part of spring A. On the other hand, frictional force was detected by the strain gages which were attached to spring B in the same way as doing to spring A.
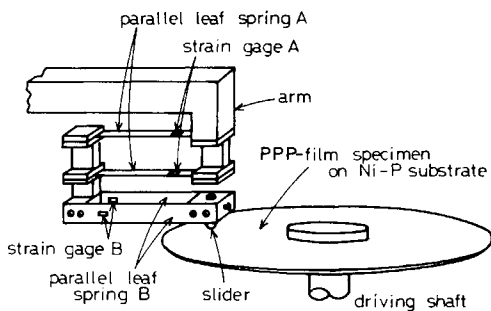
Fig. 3. Schematic of sliding friction tester.

The magnitudes of strain, induced in each sets of strain gages, were measured by a strain meter, and its outputs were recorded by a two-channel recorder. The accurately linear calibration curves were obtained for load in the range from 1–10 g for each sets of strain gages.

Friction coefficients were calculated from the ratio of friction force to load.

Read/Write Tests

Ni—Co—P medium was prepared on the substrate in the same manner as reported previously.[4] The chemical composition of it was 47% nickel, 51% cobalt, and 2% phosphorus. The film thickness of the medium was adjusted to 0.2 μm. The magnetic properties of the medium were coercivity (H_c) of 550 Oe and residual magnetic flux density (B_r) of 10,000 G.

The head used was made of Mn—Zn ferrite, with gap length of 0.5 μm, track width of 100 μm, and coil turns of 10 + 10. The floating height of the head was adjusted at about 0.4 μm. Read/write conditions were write current of 40 mA$_{pp}$ and circumferential speed of 34 m/s. PPP films, used for read/write tests, were TCy film in thickness of 1200 Å.

Contact Start/Stop (CSS) Cycle Tests

The abrasive properties of PPP films were estimated by CSS cycle tests. The CSS cycle test is the repeat of start and stop of disk rotation, whereupon the head also repeats floating and contact to the disk surface. One cycle to repeat was 9 s. The load of 9 g and the maximum circumferential speed of 18 m/s was applied to the IBM-3340 compatible head. The wearing tracks on the PPP film surface were observed after a certain number of repeats.

RESULTS AND DISCUSSION

Fundamental Properties of PPP Films

The adhesivenesses to the substrate and chemical-stabilities of PPP films were evaluated qualitatively. The results are shown in Table I. Poly(methyl methacrylate) (PMMA) film which was prepared on the substrate by the standard spin-coating technique was also evaluated in the same manner for comparison.

TABLE I
Some Fundamental Properties of PPP Films on Ni—P Substrate

PPP film	Film thickness (Å)	Peeling test		Chemicals, stability (20°C, 10 min, dipping)			Water contact angle[c]
		Scotch tape test[a]	Boiling water dipping (10 min)	Organic solvent*	10% NaOH	10% HCl	
TCy	1300	O	O	O	△	×	—
(toluene-2,4-	1600	—	—	—	—	—	68°
disocyanate)	2700	O	O	O	×	×	—
α-Pyr	1000	—	—	—	—	—	42°
(α-pyrroli-	1200	O	O	O	△	×	45°
done)	1500	O	O	O	O	×	—
	2000	—	—	—	—	—	50°
6FP	1100	O	O	O	△	△	90°
(hexafluoro-	1500	O	O	O	△	△	—
propylene)	2000	—	—	—	—	—	95°
4FE	900	O	O	O	O	×	92°
(tetrafluoro-	1200	O	O	O	O	×	—
ethylene)							
PMMA[d]	5000	×	△	e	—	—	64°

Note: (O) No change; (△) partially peeled off; (×) entirely peeled off.

[a] Films were cut up into 2 mm² before test.

[b] The solvents tested were toluene, methyl isobutyl ketone, dioxane, tetrahydrofurane, dimethyl sulfoxide, and isopropyl alcohol.

[c] Water contact angles were measured 300 hours after film preparations.

[d] PMMA-film was prepared by spin-coating.

[e] Film dissolution except for isopropyl alcohol.

The results of peeling and boiling tests were that PPP-films exhibited a good adhesion to the substrates, even though PPP films such as 6FP and 4FE films did not have a hydrogen bond. The good adhesiveness of the plasma polymerized film has been also reported by Dynes and Kaelble for styrene and epichlorohydrin on aluminum,[7] and Millard et al. for perfluorobutene-2 on glass.[8] These adhesiveness could be due to the surface cleaning effect by ion sputtering in plasma discharge and the formation of a network polymer on the substrate. Surface contamination and adsorbed water are removed in the former effect. The adhesiveness of PPP films should have an influence on frictional and lubricative properties of the protective film. PPP films showed excellent stabilities to many organic solvents, which were due to the highly crosslinked structure of the polymer. However, PPP films indicated poor durability to inorganic solvents. PMMA film revealed a good solubility to organic solvents because of its linear structure.

The large water contact angles for 6FP and 4FE films could be due to their elemental composition of carbon and fluorine, because they cannot form a hydrogen bond with water. The current data for 6FP and 4FE films are almost similar to values of 94°–98° for plasma polymerized film of perfluorobutene-2.[8] The value of 92° for the 4FE film was somewhat small compared with 108° for bulk polytetrafluoroethylene (Teflon).[8]

PPP-Film Preparations with Homogeneous Thickness

The PPP-film deposition rates (R_p) were dominantly governed by the discharge current density (I_p) and the monomer gas pressure (P_m) in the current discharge system. R_p incresed approximately proportionally to I_p. R_p also increased according to the increase of P_m in the range of 0.1–0.3 Torr. The typical film formations are shown in Figure 4. The large difference of R_p was not observed in each monomer except for 4FE. 4FE-film formations gave very small R_p by 800 kHz power supply in the P_m range of 0.1–0.3 Torr. 4FE-films with large R_p were obtained by a 13.56-MHz power supply. Its curve for thickness vs. discharge time gave a specific curve shown in Figure 4. The etching of 4FE film occured after the discharge time of 2.5 min. This result should be peculiar to 4FE in the current discharge system.

Thickness homogeneities on the radius of the substrate surface are shown in Figures 5 and 6 with regard to I_p and P_m, adjusting all other discharge conditions to constant. Thickness heterogeneity on the circumference of the substrate surface did not occur, because the substrate was rotated during discharge.

It is considered that the homogeneity of PPP films is fundamentally influenced by the diffusion of the monomer gas and active species which make the monomer polymerize, and this diffusion is governed by apparatus geometries and discharge conditions. Besides, the best discharge condition for thickness homogeneity depends on apparatus geometries. The flow rate and pressure of monomer, and the frequency and current density of discharge rf power are the main factors in discharge conditions.

The most important thing to notice in the results is that the thickness heterogeneity can be depressed within 5%, determining the optimum discharge condition, and this slight heterogeneity does not exert an aggravating influence upon head floating.
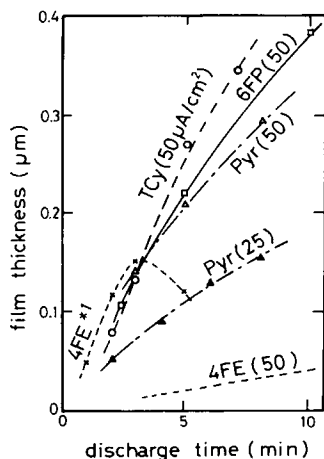

Fig. 4. Plasma polymerized protective-film deposition rates (*1) Application of 13.56 MHz rf-power supply; (O) TCy (50 μA/cm^2); ($\square$) 6FP(50); ($\triangle$) Pyr (50); ($\blacktriangle$) Pyr (25); ($\times$) 4FE (50).
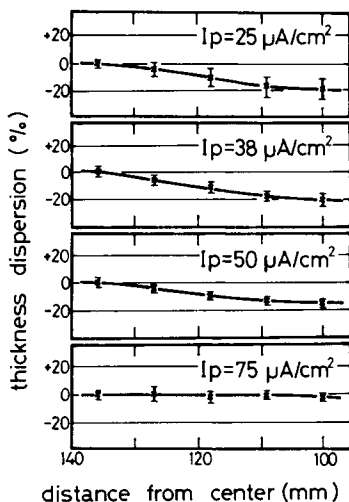
Fig. 5. Thickness homogeneity as a function of discharge current density (I_p); monomer, α-Pyr; P_m = 0.1 Torr.

Frictional Properties of PPP Films

Figure 7, 8, and 9 are friction coefficients of TCy, α-Pyr, and 6FP film as a function of film thickness. The friction coefficients of PPP films were not influenced by load in the range of 1–10 g and circumferential speed in the range of 0.5–10 cm/s. All friction coefficients were measured by load of 2 g and circumferential speed of 1 cm/s.

It was evident that the friction coefficient of PPP films increases in the thickness range below ca. 1500 Å, and the friction coefficients of PPP film almost show similar values from 0.3 to 0.4 in the thickness range above ca. 1500 Å.

It is well known that good lubrication and small friction by thin films on hard metals are due to the small shear strength of thin films. The friction coefficients
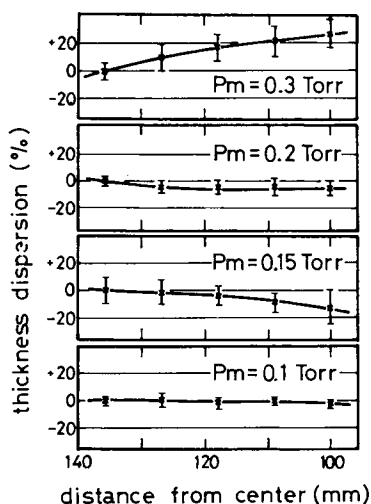
Fig. 6. Thickness homogeneity as a function of monomer gas pressure (P_m); monomer, α-Pyr; I_p = 75 μA/cm².
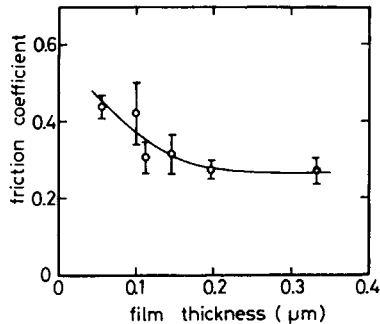
Fig. 7. Friction coefficient of TCy films on Ni—P substrate as a function of film thickness; load, 2 g; friction speed, 1 cm/s.

of 0.3 ~ 0.4 above ca. 1500 Å show, however, somewhat large values, compared with that of bulk polymers, although PPP films are composed of hydrocarbon or fluorocarbon.   It can be considerd that the large friction coefficients of PPP films are responsible for the somewhat large shear strength of PPP films because of the highly crosslinked structure of the polymer.   The friction coefficients of 0.3 ~ 0.4 in the thickness above ca. 1500 Å were of slightly different values depending on the kind of monomer, when compared with that for bulk polymers, e.g., 0.1 for Teflon[9] and 0.4 ~ 0.6 for polyimides.[9]   This is also attributed to highly
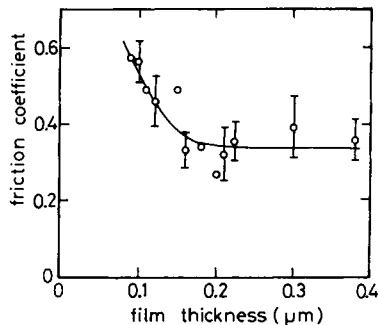

Fig. 8. Friction coefficient of α-Pyr films on Ni—P substrate as a function of film thickness; load, 2 g; friction speed, 1 cm/s.
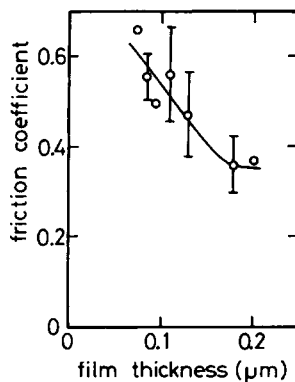

Fig. 9. Friction coefficient of 6FP films on Ni–P substrate as a function of film thickness; load, 2 g; friction speed, 1 cm/s.

crosslinked structure of the polymer, because the degrees of crosslinking are not so different in the kind of monomer.

Bowden and Taber have also reported that the friction coefficient of an indium-lubricated steel surface shows the thickness effect similar to Figures 7, 8, and 9.[10] They explained that high friction coefficients at very small film thickness were caused by nonuniform deposition of the plated soft metal, which allows easy rupture of the film during sliding. The same results on PPP films are only caused by rupture of PPP films because high thickness homogeneity of PPP films is obtained, described above. TCy films showed relatively low friction coefficients at a very small thickness, compared with that of 6FP and α-Pyr films. It seems to suggest that TCy films do not easily rupture.

Figures 10(a)–(d) show the microscopic pictures of the wearing track on PPP film after one-time friction of the slider. Figure 10(e) shows that of spin-coated PMMA film. TCy and α Pyr films show a good adhesion to the substrate, compared with the poor adhesion of PMMA film, even if the load for TCy film is 6 g. 4FE and 6FP film do not give so good adhesion, because the substrates are revealed partially in the wearing track.

Read/Write Tests

The read/write property of the plated disk is shown in Figure 11, in which TCy film in thickness of 1200 Å is applied. The result indicates the recording density of about 620 bit/mm from megaflux reversal/mm at half output voltage, which is estimated to be almost the same value without PPP film, taking into account the floating height of the head. It has become, therefore, apparent that magnetic deterioration and instability do not occur by the process of plasma polymerization. Besides, PPP films do not have a bad influence on the functions of the plated disk.

Contact Start/Stop (CSS) Cycle Tests

The results of CSS cycle tests are shown in Table II. PPP films showed a tendency to generate easily a surface cut in the early state of CSS cycle tests. These surface cuts did not have fatal influences on head floating and the protection of magnetic medium. PPP films in relatively small thicknesses exhibited a good CSS durability, as opposed to the frictional properties.

The unstable head floating and the state in which the head did not float were caused by the invasion of the fragments of peeled protective films to the gap between the disk surface and the head. It is, therefore, considered that PPP films in large thickness generate the large fragments of the peeled protective film, and it easily makes the floating head instable.

6FP and 4FE films show relatively low CSS durability, even though the surface-cut generation is late. Generally, fluorocarbon polymers such as Teflon have superior frictional and lubricative properties, but they show poor adhesiveness to every substrate. 6FP and 4FE films should have relatively small adhesiveness, compared with TCy and α-Pyr films, even though the same results for peeling tests are obtained. Once the surface cut generates on the 6FP or 4FE film surface, the films are peeled easily; they then generate many film fragments. On the other hand, TCy films in thickness of ca. 1000 Å indicate good CSS du-
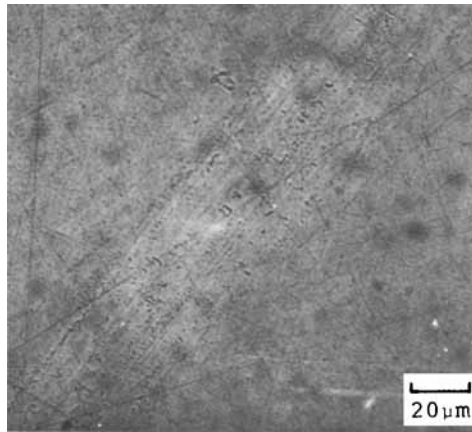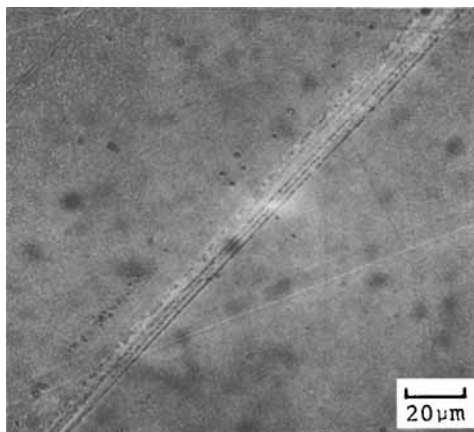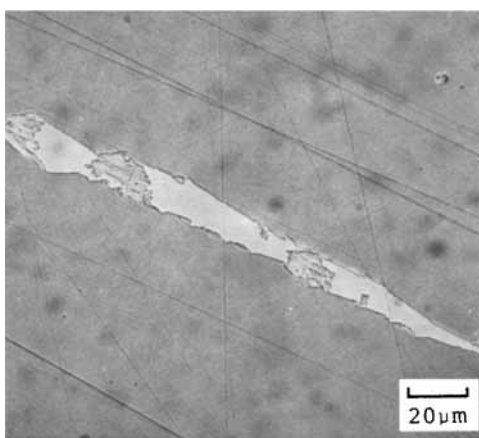
(a)
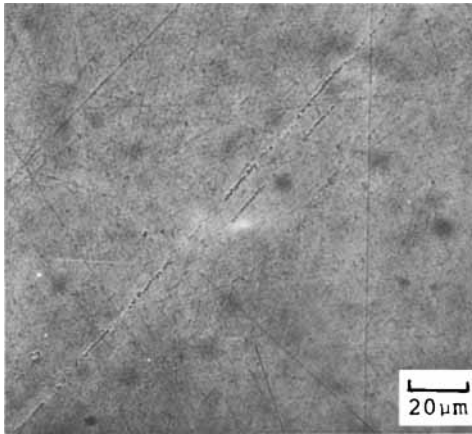
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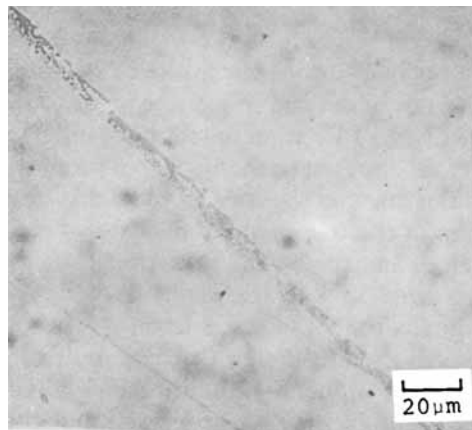
(c)

Fig. 10. Microscopic pictures of wearing track on PPP film (a) TCy film (film thickness, 1300 Å; load, 6 g); (b) α Pyr film (1200 Å, 2 g); (c) 6FP film (1500 Å, 2 g); (d) 4FE film (1200 Å, 2 g); (e) PMMA film, prepared by spin-coating (5000 Å, 2 g).

(d)

(e)

Fig. 10. (*Continued from previous page.*)

rability, which is attributed to the good adhesiveness of TCy films to the metal substrates. It is known that isocyanate groups which exist in the TCy monomer can form urethane bonds, reacting to hydroxyl groups of metal surface, and it gives a strong adhesion with metals.[11]
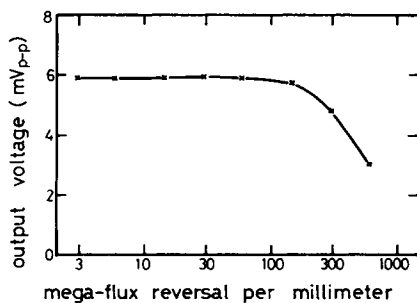

Fig. 11. Output voltage vs mega-flux reversal per second for Ni–Co–P medium, applied TCy film in thickness of 1200 Å.

TABLE II
Results of Contact Start/Stop (CSS) Cycle Tests for PPP Films

PPP-film	film thickness (Å)	10^1	CSS cycle 10^2	10^3	10^4
TCy	1000	O			
	1200	O			
	2000			□△	
	2500			□△	
αPyr	1000	O		□	
	1200		O		□
	2000	O	×		
	2800	O			□
6FP	1100		O		□
	1500		O		×
	2000		O	□	
4FE	900		□×		
	1200		□×		
no PPP-film		O	×		

Note: (O) Surface-cut generation; (□) partial peeling of PPP film; (△) instable head flying; (×) head did not fly.

It has become apparent that the adhesion of PPP films to the substrate is the most important factor for CSS durability. PPP films in relatively small thicknesses near 1000 Å give good protective films.

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