Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Characterization of Polymer Thin Films Sputtered onto a Copper Substrate with Two Kinds of Polyimide Targets

Satoru Iwamori [a], Kazuya Kezuka [a] & Akihiro Uemura [a b]

[a] Division of Innovative Technology and Science, Graduate School of Natural Science and Technology, Kanazawa University, Kakumamachi, Kanazawa, Japan

[b] Nakai Techno Co., Ltd., Miyake-cho, Shiki-gun, Nara, Japan

Version of record first published: 22 Sep 2010

To cite this article: Satoru Iwamori, Kazuya Kezuka & Akihiro Uemura (2007): Characterization of Polymer Thin Films Sputtered onto a Copper Substrate with Two Kinds of Polyimide Targets, Molecular Crystals and Liquid Crystals, 471:1, 99-111

To link to this article: http://dx.doi.org/10.1080/15421400701545411

Mol. Cryst. Liq. Cryst., Vol. 471, pp. 99–111, 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701545411

Characterization of Polymer Thin Films Sputtered onto a Copper Substrate with Two Kinds of Polyimide Targets

Satoru Iwamori
Kazuya Kezuka
Division of Innovative Technology and Science, Graduate School of Natural Science and Technology, Kanazawa University, Kakumamachi, Kanazawa, Japan

Akihiro Uemura
Division of Innovative Technology and Science, Graduate School of Natural Science and Technology, Kanazawa University, Kakumamachi, Kanazawa, Japan; Nakai Techno Co., Ltd., Miyake-cho, Shiki-gun, Nara, Japan

Polymer thin films were sputtered with two kinds of polyimide (PI) targets, pyromellitic dianhydride-oxydianiline (PMDA-ODA) and biphenyl dianhydride-p-phenylene diamine (BPDA-PDA), onto a copper substrate by a conventional RF sputtering with argon (Ar) and nitrogen (N_2). These polymer thin films were characterized, and their adhesion and tribological properties were evaluated.

Sputtering rate of the polymer thin film with PMDA-ODA target (sputtered PMDA-ODA thin film) with Ar was higher than that with BPDA-PDA target. Although the sputtering rate of the polymer thin film with the BPDA-PDA target (sputtered BPDA-PDA thin film) with Ar showed highest value at a pressure of 5 mTorr, that with N_2 showed highest value at a pressure of 60 mTorr. Nitrogen content in the sputtered BPDA-PDA thin film with N_2 increased compared to that of the sputtered BPDA-PDA thin film with Ar and target material (pristine).

Although friction coefficients of these sputtered BPDA-PDA thin films with Ar were almost the same as those of the pristine PIs, that of the sputtered BPDA-PDA thin film with N_2 was much higher than that of the pristine BPDA-PDA. The wear durability of the sputtered PMDA-ODA thin film with Ar was slightly higher than that of sputtered BPDA-PDA thin film. The wear durability of the sputtered BPDA-PDA thin film with N_2 was much higher than that of the polymer thin film sputtered with Ar.

The authors would like to thank Mr. Itsuo Nishiyama of DAIPLA WINTES CO. LTD for adhesion strength measurement of sputtered thin films with SAICAS.

Address correspondence to Satoru Iwamori, Division of Innovative Technology and Science, Graduate School of Natural Science and Technology, Kanazawa University, Kakumamachi, Kanazawa, Japan. E-mail: iwamori@t.kanazawa-u.ac.jp

The adhesion strength between the sputtered BPDA-PDA thin film with N_2 and copper substrate was higher than that between the thin film sputtered with Ar and copper substrate. In addition, the sputtered BPDA-PDA thin film with N_2 was introduced between the copper substrate and the sputtered BPDA-PDA thin film with Ar (Ar/N_2 laminate). The adhesion strength of this laminate was higher value than that between the sputtered BPDA-PDA thin film with Ar and copper substrate.

Keywords: adhesion strength; copper substrate; friction coefficient; polyimide; RF sputtering; thin film, wear durability

1. INTRODUCTION

Polyimides (PIs) possess excellent thermal stability, chemical stability and mechanical properties. PI films are often used as an insulator in print circuit boards (PCBs). So many researchers have attempted to improve the adhesion strength between copper thin films and PI substrates. Recently, a PI thin substrate, as well as the copper thin film, is expected in the microelectronic industry. RF sputtering is one of the effective methods for depositing PI thin films on a substrate.

Sputtering is widely used in electrical and mechanical industries, because a sputtered thin film has a uniform structure and an excellent adhesion property to most substrates. Polymer thin films prepared by the sputtering with PI and poly(tetrafluoroethylene) (PTFE) targets have been reported since the 1970s and their tribological properties have been characterized. Polymer thin films sputtered with PI targets were deposited onto metal and glass substrates, and their morphologies and tribological properties were evaluated [1–6]. These polymer thin films are thought to have a disadvantage for the manufacture on industrial scale because the sputtering rate of the thin films is much lower than that of the polymer thin film with the PTFE target. But the tribological properties, such as low friction coefficient and high wear durability, of the polymer thin films sputtered with the PI target are better than those with the PTFE target [2]. The reason why the polymer thin film sputtered with the PI target has higher wear durability compared to the thin film sputtered with the PTFE target is thought to be due to its high adhesion strength to the substrate [2]. We characterized the polymer thin films prepared by RF sputtering with two kinds of PI targets, PMDA-ODA and BPDA-PDA, and evaluated their adhesion strength to a copper substrate, as well as their tribological properties [7–9]. In this paper, we evaluate molecular structures, adhesion and tribological properties of the polymer thin

films prepared by the RF sputtering with PI targets. This article would be a first report on the molecular structures of the polymer thin films prepared by RF sputtering.

2. EXPERIMENTALS

Two kinds of PIs, Kapton-V^{TM} (PMDA-ODA: 200 μm thick, Toray-DuPont Chemicals, Japan) and Upilex-S^{TM} (BPDA-PDA: 125 μm thick, Ubekosan, Japan), were used for sputtering targets. Figure 1 shows the molecular structures of these PI targets. Glass slides and copper plates (60 mm square, 2.5 mm thick) were used as the substrates. Glass slide substrates were used for the measuring sputtering rate and chemical bonding states of the polymer thin films prepared by the RF sputtering. The copper substrates were used for evaluation of the adhesion and tribological properties. The copper plates were polished with different grades of sandpaper (#400, #800, #2000). An arithmetical mean roughness (Ra) of the copper surfaces was measured using a surface roughness measurement instrument, Surfcom 1400A-6^{TM}(Tokyo Seimitsu, Inc., Japan). The Ra value was 50 nm after these procedures. These polished substrates were washed with distilled water and ultrasonically cleaned in acetone.

Polymer thin films were sputtered onto these substrates with PI targets with argon gas. After the sputtering chamber was evacuated to a pressure of 1.0×10^{-5} Torr, the pressure in the chamber was kept between 2 and 80 mTorr by adjusting the main valve installed in the sputtering system. The thickness of these polymer thin films was determined by measuring the heights between the film and glass slide with a profilometer, Surfcom 1400A-6^{TM} (Tokyo Seimitu, Inc., Japan). The thickness of the thin films used for evaluation of wear durability and adhesion strength was 1.0 μm.

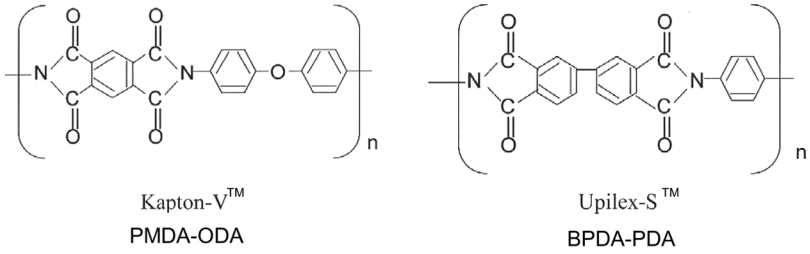

FIGURE 1 Molecular structures of PI targets.

The composition and chemical bonding states of these polymer thin films were determined by x-ray photoelectron spectroscopy (XPS) (Quantum2000: Phi Co) using Al Kα radiation with an energy of 1486.6 eV. The chemical bonding states were also analyzed with fourier transform-infrared (FT-IR) spectroscopy measurement. These polymer thin films peeled off from the glass slide substrate were embedded in KBr pellets and were analyzed by using a FT-IR spectroscope model 610 (JASCO International Co.). Absorption in the range 2100–600 cm^{-1} was measured.

A pin-on-disk type friction and wear test apparatus with a bearing steel ball (1 mm in diameter) as the slider was used for evaluation of friction coefficient and wear durability [7,9]. Revolution speed of the disk was 5 revolutions/min and revolution diameter of the pin was 8 mm. The load on the bearing steel ball was 20 g for measuring friction coefficient, and 50 g for evaluation of wear durability. The wear durability was evaluated by measuring the extent of peeling as shown in Figure 2. When a polymer thin film is worn or peels off from the copper substrate, an electric current flows between the pin and the substrate (Fig. 2) [7].

The adhesion strength between the polymer thin films and copper substrate was measured with two methods. A stud (6 mm in diameter) was bounded to the polymer thin films with an epoxy resin. The adhesion strength was determined by the pulling the stud using Tensilon^{TM} (Touyou Sokuki Inc., Japan) [7–9]. The pull speed was 0.01mm/min. Another method to measure the adhesion strength

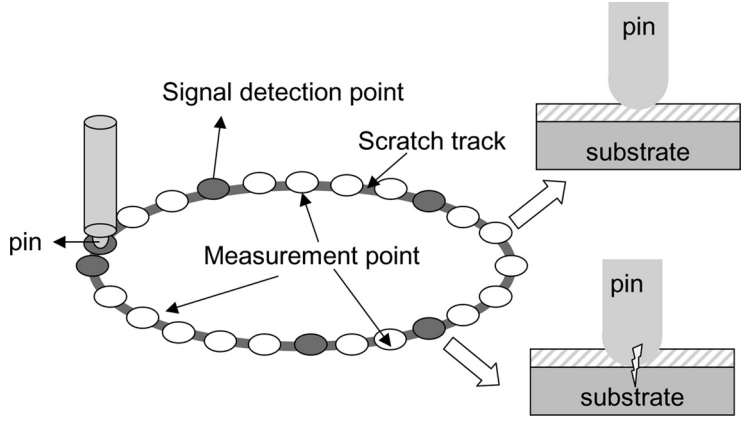

FIGURE 2 Schematic diagram how to measure the extent of wear.

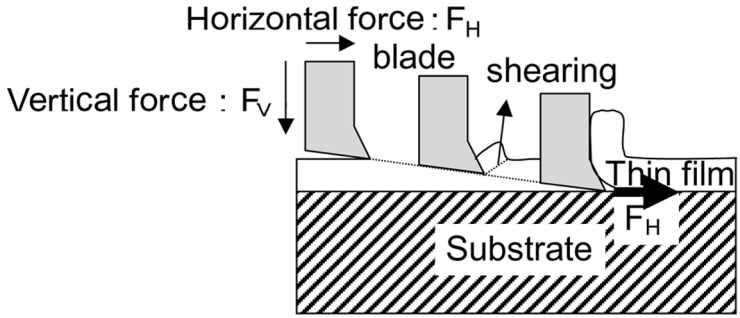

FIGURE 3 Schematic diagram of the SAICAS.

between the polymer thin film and copper substrate was SAICAS (Surface and Interface Cutting Analysis System: Daipla Wintes Co.). Figure 3 shows a schematic diagram of SAICAS. Vertical and horizontal reaction forces at a single crystal diamond blade during cutting the thin film were monitored. After tip of the blade gets to the interface between the thin film and substrate, it moves to the horizontal direction. This force means the adhesion strength between the thin film and substrate. The adhesion strength P can be represented as follows [10];

$$P = F_H/w \quad (kN/m) \tag{1}$$

F_H and w denote the horizontal reaction and width of the blade.

3. RESULTS AND DISCUSSIONS

3.1 Polymer Thin Films Sputtered with PI Targets

Figure 4 shows the relationship between sputter rates and pressures during the sputtering with PMDA-ODA (Kapton-V^{TM}, Toray-DuPont Chemicals, Japan) and BPDA-PDA (Upilex-S^{TM}, Ubekosan, Japan) targets. Although both of the sputtering rates of these polymer thin films slightly increased with increase of pressure up to 5 mTorr, they decreased with increase of pressure beyond 5 mTorr. The sputtering rate of the sputtered BPDA-PDA thin film was higher than that of the sputtered PMDA-ODA thin film at all pressures up to 60 mTorr. Taking into consideration that polymer thin film sputtered with PTFE target (sputtered PTFE thin film) deposited at 10 mTorr was 45 nm/min, the sputtering rates of these polymer thin films are much lower than that of the sputtered PTFE thin film [11]. Figure 5 shows a photograph of the sputtered BPDA-PDA thin film isolated from the

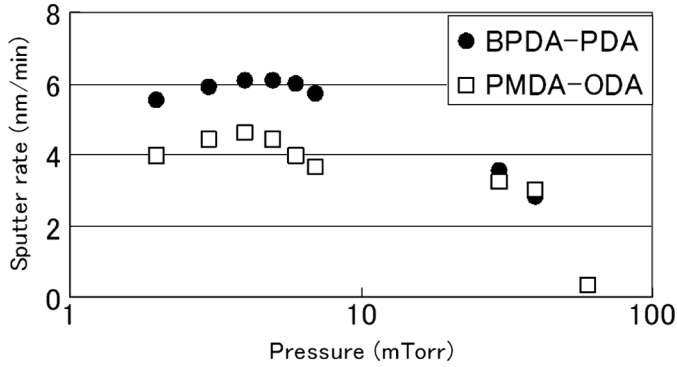

FIGURE 4 Sputter rate versus pressure for the polymer thin films with PI target.

glass slide substrate. Thickness of the thin film was 1 μm, and it was almost the same morphology as the pristine BPDA-PDA target. Table 1 shows elemental composition (At%) and area (%) of peaks from C(1s) XPS spectra of the pristine PIs and polymer thin films sputtered with Ar. Carbon contents of these polymer thin films increased, but oxygen and nitrogen contents decreased compared to those of the pristine PIs. Peak 2, which represents C–N or C–O moieties,

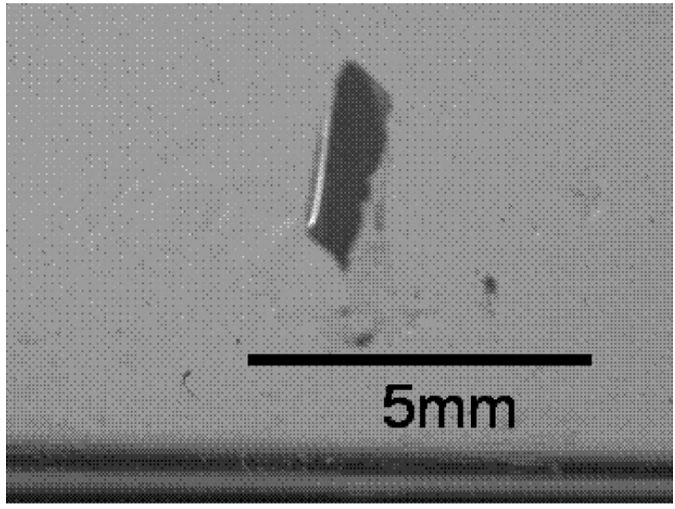

FIGURE 5 Photograph of the sputtered BPDA-PDA thin film with Ar isolated from the glass slide substrate.

TABLE 1 Elemental Composition (At%) and Area (%) of Peaks from C(1s) XPS Spectra of the Pristine PIs and Sputtered PI Thin Films

	Oxygen	Nitrogen	Carbon	Peak 1 (C−C)	Peak 2 (C−N, C−O)	Peak 3 (C=O)
PMDA-ODA (Pristine)	17	7	76	63.0	26.7	10.3
PMDA-ODA thin film	13	5	82	83.8	7.3	8.9
BPDA-PDA (pristine)	14	7	79	72.5	22.7	4.8
BPDA-PDA thin film	9	4	87	83.7	10.9	5.4

decreased considerably, but that of the peak3, which represents C=O moiety, is almost at the same level as those of pristine PIs from the results of XPS analyses [7]. We reported earlier that the nitrogen atom in the imide moiety and the oxygen atom in the ether moiety in the PI structure easily reacted with radicals [12]. We think that imide (C−N) and diphenylether (C−O) moieties in the PI structure would be attacked and cleaved by the argon radicals in the argon plasma. This is one of the reasons why the peak 2 in the polymer thin films sputtered with the PI targets decreased compared to those in the pristine PIs [7].

Nitrogen (N_2), and argon and nitrogen mixture ($Ar + N_2$) were introduced into the sputtering chamber for the sputtering gases. Sputtering rate of the sputtered BPDA-PDA thin film with Ar showed highest value at a pressure of 5 mTorr. However, the sputtering rate with nitrogen gas showed highest value at a pressure of 60 mTorr. Nitrogen content in the thin film sputtered with the nitrogen (N_2) gas increased compared to that sputtered with argon (Ar) gas and target material (Upilex-S^{TM}) (Fig. 6) [9]. Figures 7(a) and (b) show C(1s)XPS spectra of the sputtered BPDA-PDA thin film with Ar and N_2, respectively [9]. Peak intensity of peak 2 in Figure 7(b) increased considerably compared to that in Figure 7(a). Figure 8 shows FT-IR spectra of the pristine BPDA-PDA, sputtered BPDA-PDA thin films with Ar and N_2, respectively. Absorption peaks at 1780, 1720 and 1380 cm^{-1} represent imide moiety, and the peak at 1500 cm^{-1} represents benzene ring in the PI structure. These peaks can be clearly recognized only in the pristine BPDA-PDA spectrum. However, a large and broad peak around 1000–1800 cm^{-1} can be found in the spectrum of the sputtered BPDA-PDA thin film with N_2. Although peak intensity of the spectrum of the sputtered BPDA-PDA thin film with Ar is lower than that of the sputtered thin film with N_2, a broad peak can also found. These peaks around 1000–1800 cm^{-1} mean that there are wide varieties of chemical bonding states in these thin films. Lee *et al*. reported the FT-IR spectrum of a PI thin film prepared by a

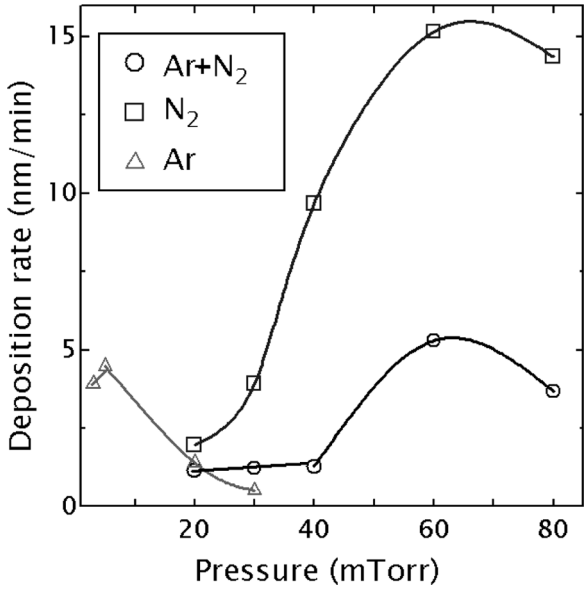

FIGURE 6 Sputter rate versus pressure for the sputtered BPDA-PDA thin films [9].

vacuum deposition polymerization [13]. Maggioni *et al*. also reported the spectrum of a PI thin film prepared by a glow discharge deposition polymerization [14]. The absorption peaks, which represent the imide moiety and benzene ring, were clearly found in these PI thin films as well as pristine PI. Although these deposition methods belong to the vapor deposition as well as the sputtering, they contain a process of polymerization reaction with heating. These absorption peaks are not clearly found in the FT-IR spectra of the sputtered BPDA-PDA thin films with Ar and N_2, because RF sputtering with PI targets does not contain the process. Figure 8 also shows that there are various chemical bonding in the sputtered BPDA-PDA thin films with Ar and N_2, because sputtered PI molecules are decomposed and recombine due to the plasma. Choukourov *et al*. reported the polyimide-like thin films deposited by thermal degradation of polyimide with and without simultaneous activation by a glow discharge exited using an r.f. planar magnetron [15]. Remarkable peaks around 1000–1800 cm^{-1} in the FT-IR spectra became broader and disappeared with increase of the r.f. power. In addition, contact angles of water on the deposited films decrease with increase of the r.f. power, which means that concentration of hydroxyls increased [15]. C(1s) XPS spectra of

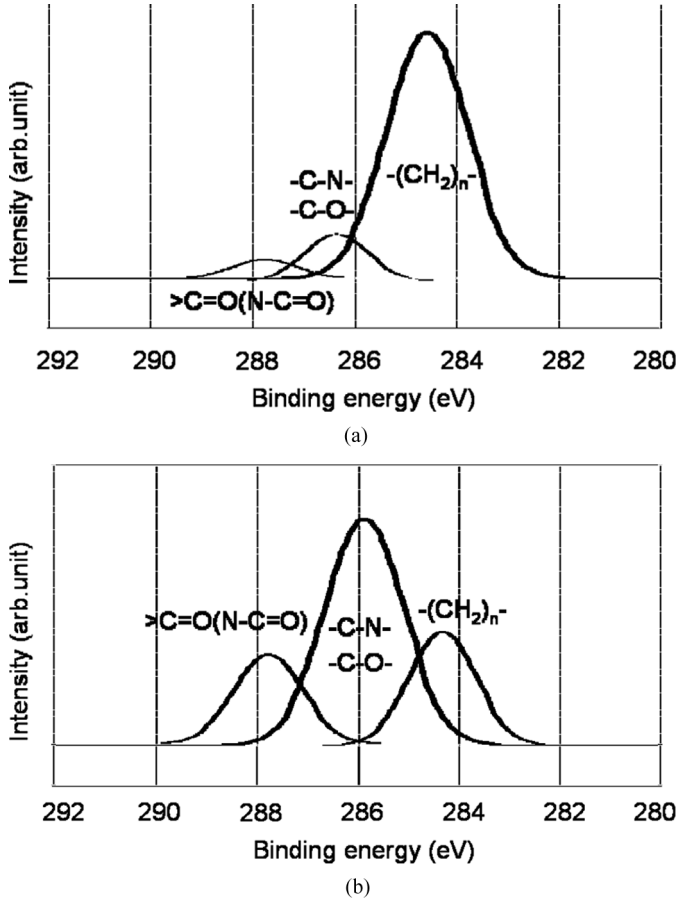

FIGURE 7 C(1s)XPS spectra of the sputtered BPDA-PDA thin films with Ar (a) and N_2 (b) [9].

these polymer thin films, as shown in Figure 7, were separated three peaks, peak 1 to 3, respectively [9]. However, in fact, these peaks contain various chemical bonding, in addition to CH_2 (peak 1), C−N, C−O (peak 2) and C=O (peak 3) shown in Figure 7. So we think, in a strict sense, the sputtered thin films do not belong to polyimde.

3.2. Adhesion and Tribological Properties of Polymer Thin Films Sputtered with PI Targets onto Copper Substrate

Table 2 shows the friction coefficients of the sputtered polymer thin films sputtered with PI targets onto the copper substrate. The friction

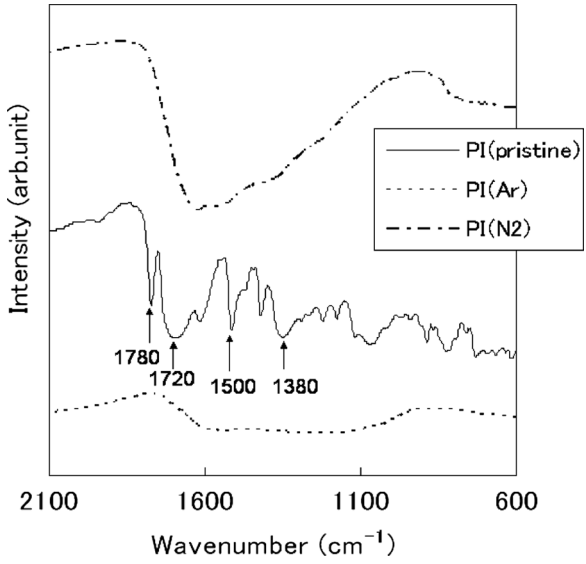

FIGURE 8 FT-IR spectra of the sputtered BPDA-PDA thin films with Ar and N_2 and pristine BPDA-PDA.

coefficients of these sputtered thin films with Ar were almost the same as those of the pristine PIs. An arithmetical mean roughness (Ra) of the sputtered BPDA-PDA thin film with Ar onto a glass slide substrate was 3 nm, and this is almost the same roughness as the glass slide. We think this is one the reasons why the sputtered PI thin films with Ar had excellent friction coefficient. Friction coefficient of the sputtered BPDA-PDA thin film with N_2 was more than twice higher than that of the thin film sputtered with Ar [8,9]. Figure 9 shows the wear durability of the sputtered PMDA-ODA and BPDA-PDA thin films onto the copper substrate [7–9]. Figure 9 shows the extent of wear after 50 and

TABLE 2 Friction Coefficient of the Pristine PIs and Sputtered PI Thin Films

	Friction coefficient
PMDA-ODA (pristine)	0.21
PMDA-ODA (Ar-sputter)	0.20
BPDA-PDA (pristine)	0.15
BPDA-PDA (Ar-sputter)	0.16
BPDA-PDA (N_2-sputter)	0.40

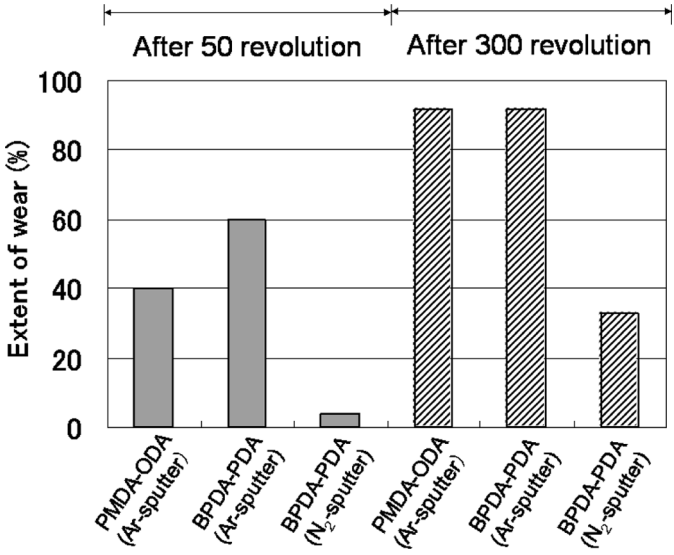

FIGURE 9 Extent of wear of polymer thin films after 50 and 300 revolutions black and hatched bars show the extent after 50 revolution and 300 revolutions, respectively.

300 revolutions. The sputtered PMDA-ODA thin film with Ar had slightly higher durability than that of the sputtered BPDA-PDA thin film with Ar. From the observation of the scratch tracks in both sputtered thin films with Ar, their wear modes were different [7]. The area peeled from the copper substrate for the sputtered BPDA-PDA thin film with Ar is much larger than that for the sputtered PMDA-ODA thin film [7]. Further, the wear durability of the sputtered BPDA-PDA thin film with N_2 was much higher than that of the sputtered thin film with Ar.

The adhesion strength between the sputtered BPDA-PDA thin films and copper substrate was estimated with a stud (6 mm in diameter) bounded to the thin films with an epoxy resin (Fig. 10). The dotted line in Figure 10 means the adhesion strength between the adhesive (epoxy resin) and thin films. The adhesion strength between the sputtered BPDA-PDA thin film with N_2 and copper substrate was higher than that between the sputtered thin film with Ar and copper substrate. Figure 10 also showed the adhesion strength of the sputtered BPDA-PDA thin film with Ar and N_2 mixture ($Ar + N_2$). It was also higher than that of the sputtered thin film with Ar. In order to improve the adhesion strength between the sputtered thin film with

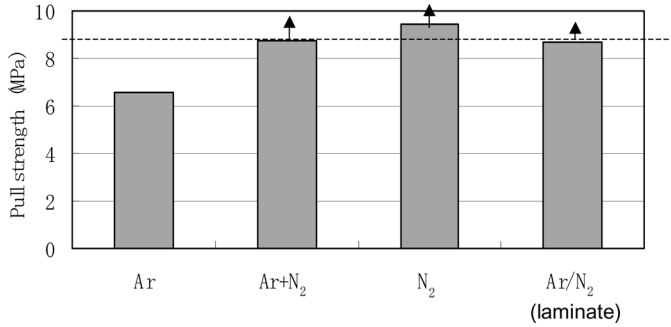

FIGURE 10 Pull strength between the copper substrate and sputtered BPDA-PDA thin films with Ar and N_2 [9] Dotted line shows the adhesion strength between the adhesive and these thin films.

Ar and copper substrate, the sputtered thin film with N_2 was introduced between the sputtered thin film with Ar and copper substrate (Ar/N_2 laminate). The adhesion strength of this laminate showed higher value than that between the sputtered thin film with Ar and copper substrate [9].

In order to estimate adhesion strength between the sputtered BPDA-PDA thin film with N_2 and copper substrate, it was measured with a SAICAS as shown in Figure 3. The adhesion strength of the sputtered thin film with N_2 was almost two times higher that with Ar (Figure 11). We reported the surface free energy of the sputtered thin film with N_2 was higher than that of the thin film with Ar [9]. This high adhesion strength would relate with the high surface free energy given by hydrophilic groups. They may appear in the peak 2 shown in Table 1 or peaks around 1800–1000 cm^{-1} shown in Figure 8.

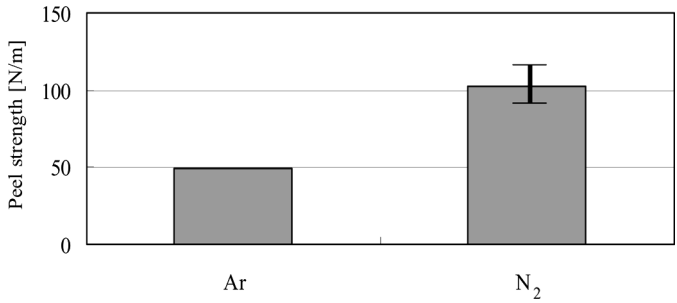

FIGURE 11 Adhesion strength of the polymer thin films to copper substrate measured with the SAICAS.

4. CONCLUSION

- Polymer thin films were sputtered onto the copper substrate with two kinds of PI targets, and evaluated adhesion and tribological properties;
- Chemical bonding states of these sputtered thin films were different from the pristine PIs.
- Although friction coefficients of the thin films sputtered with Ar were almost the same value as those of the pristine PIs, that of the thin film sputtered with N_2 was higher.
- The sputtered PMDA-ODA thin film with Ar had slightly higher wear durability than that of the sputtered BPDA-PDA thin film with Ar. The wear durability of the sputtered BPDA-PDA thin film with N_2 was much higher than that of the sputtered thin film with Ar.
- The adhesion strength between the sputtered thin film with N_2 and copper substrate was almost two times higher than between the sputtered thin film with Ar and copper substrate.

REFERENCES

[1] Kitoh, M. & Honda, Y. (1995). *Thin Solid Films*, *271*, 92.
[2] Yamada, Y., Tanaka, K., & Saitoh, K. (1990). *Surface Coatings Technology*, *43/44*, 618.
[3] Hishmeh, G. A., Barr, T. L., Sklyarov, A., & Hardcastle, S. (1996). *J. Vac. Sci. Technol.*, *A14*, 1330.
[4] Biederman, H. (1981). *Vacuum*, *31*, 285.
[5] Marechal, N. & Pauleau, Y. (1992). *J. Vac. Sci. Technol.*, *A10*, 477.
[6] Biederman, H., Zeuner, M., Zalman, J., Bilkova, P., Stelmasuk, V., & Boldyreva, A. (2001). *Thin Solid Films*, *392*, 208.
[7] Iwamori, S., Uemura, A., & Yamada, Y. (2004). *J. Adhes. Sci. Technol.*, *18*, 1771.
[8] Iwamori, S. & Uemura, A. (2004). *Materials Science and Technology*, *41*, 326.
[9] Iwamori, S. & Uemura, A. (2006). *J. Adhes. Soc. Jpn.*, *42*, 89.
[10] Nishiyama, I. & Saito, M. (2005). *J. Printing Sci. and Technol. Jpn.*, *42*, 285.
[11] Nagayama, Y., Iwamori, S., & Yamada, Y. (2003). *J. Vac. Soc. Jpn.*, *46*, 827.
[12] Iwamori, S., Yanagawa, N., Sadamoto, M., Nara, R., & Nakahara, S. (2003). In: *Polyimides and Other High Temperature Polymers*, Vol. 2, Mittal, K. L. (Ed.), VSP:Utrecht, p. 407.
[13] Lee, B. J., Kim H. G., & Lee, D. C. (2002). *Surface Coatings Technology*, *150*, 182.
[14] Maggioni, G., Carturn, S., Rigato, V., & Mea, G. D. (2001). *Surface Coatings Technology*, *142/144*, 156.
[15] Choukourov, A., Hanuš, J., Kousal, J., Grinevich, A., Pihosh, Y., Slavínská, D., & Biederman, H. (2006). *Vacuum*, *80*, 923.