

Scratch Resistant Low Friction/Low Surface Energy Coating for Silicon Substrate

H. H. CHEN, *IBM Corporation, General Products Division,
6300 Diagonal Highway, Boulder, Colorado 80301-9191*

Synopsis

A smooth, ultrathin film of a polydimethylsiloxane (PDMS) on a silicon substrate has been prepared by spin-coating. This film gives a 0.06 dynamic coefficient of friction against paper, the lowest value ever reported for polymer-paper sliding pairs. The value is only about one-third of the coefficient of friction (0.21) between polytetrafluoroethylene and paper. The coating is not scratchable by sliding a stainless steel stylus over the surface with a pressure greater than 3.6×10^{10} dyn/cm². The film displays a surface tension of 20.5 dyn/cm. It is stable in water and propylene glycol. The film is an effective and durable solid lubricant. The surface characteristics of a spray-coated PDMS and a plasma-copolymerized thin film of perfluoropropane and 3,3,3-trifluoropropylmethyldimethoxysilane have also been investigated. Both films show much lower scratch resistance, weaker adhesion to the silicon substrate, and higher friction. The plasma film yields the same surface tension as the spin-coated PDMS. Its surface energy, however, increases after soaking in water or propylene glycol. The exceptionally low friction and the unusually high scratch resistance of the ultrathin film of PDMS are attributed to the absence of deformation and tearing components and a low adhesion component in the sliding friction mechanism.

INTRODUCTION

An ink jet printer with a multinozzle print head has the potential of high-speed, high-quality, and extremely quiet printing. The nozzle plate is usually made of metal or silicon and has small orifices, e.g., 1–100 μm in diameter. The silicon is usually etched by photolithography.^{1–3} Because both silicon and metal substrates have high surface energies, the ink tends to spread on the surface of the nozzle plate. This causes misdirection of ink jets and results in poor-quality print. The problem can be solved by applying a durable, hydrophobic coating to the surface of the nozzle plate.

This paper describes the preparation and comparison of properties of protective coatings for ink jet nozzle plates or semiconductor/electrooptic devices. The coatings include polydimethylsiloxane (PDMS) films and a plasma-polymerized copolymer of perfluoropropane (PFP) and 3,3,3-trifluoropropylmethyldimethoxysilane (TFPS).

An ultrathin film of PDMS displays all of the characteristics of an ideal protective coating. These characteristics are strong adhesion to a substrate, high scratch resistance, low friction, low surface energy, and long-term stability.

EXPERIMENTAL

Materials

3,3,3-Trifluoropropylmethyldimethoxysilane (TFPS). Petrarch Systems.

Perfluoropropane (PFP). Matheson.

Polydimethylsiloxane A Prepolymer. A mixture of silanol-terminated PDMS prepolymer and multifunctional-silanes containing amino groups.

Polydimethylsiloxane B Prepolymer. A mixture of approximately 90% PDMS prepolymer containing vinyl groups, 10% hydrogen-functional PDMS crosslinker, and a small amount of platinum catalyst.

Silicon Wafer. (1.5 in. diameter, both thermally oxidized and not oxidized). Aurel.

Coating Processes

Spin Coatings. Two drops of 0.3–0.5% solution of polydimethylsiloxane (PDMS) in methylethyl ketone (MEK) were applied to a silicon wafer mounted on a Headway Research Model EC101 photoresist spinner. The wafer was immediately spun at 3000 rpm for about 10 s. Then the sample was cured at appropriate temperatures; PDMS-A was cured at room temperature for 30 min and PDMS-B at 190°C for 30 min.

Spray Coating. A 5% solution of polydimethylsiloxane in MEK was sprayed onto a silicon wafer, using a Zicon Model 1000 sprayer. The sample was cured under the conditions described above.

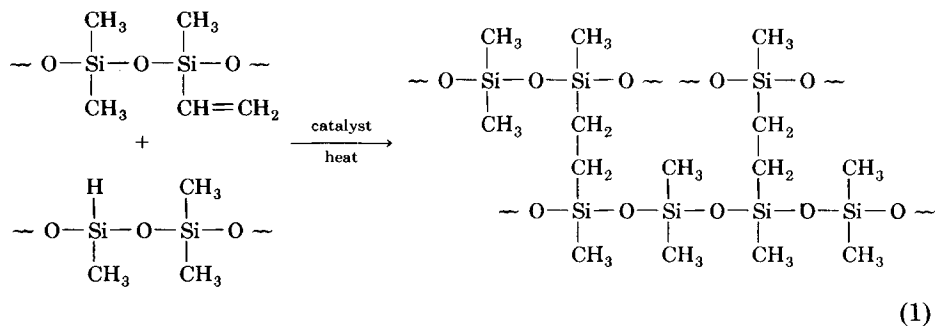
Plasma Coating. All of the plasma-polymerized films were prepared by M. Ries and L. Bruning of IBM Boulder. Plasma polymerizations were carried out in a glow-discharge environment, using a Plasma-Therm Systems Model 2484 etch system. The films were prepared in a parallel-plate radial-flow reactor, operating at a pressure of 100 mTorr, a radio frequency of 13.56 MHz, and a temperature of 80°C. The RF power was between 225 and 750 W. Argon was used as a diluent and was allowed to flow continuously during the process. The process⁴ consisted of the following steps:

1. The TFPS monomer was introduced into the reaction chamber.
2. A film was allowed to grow on a silicon wafer for 10 min.
3. The PFP monomer was introduced and allowed to copolymerize with the TFPS for 10 min.
4. The TFPS flow was turned off, and a PFP film was allowed to grow on the top surface of the wafer for 1 min.

Polymerization

The general mechanism of plasma polymerization is discussed in detail in the literature.^{5–7} PDMS-A is a mixture of silanol-terminated PDMS prepolymer and multifunctional silane crosslinkers containing amino groups. The amino groups are attached to the silicon atoms of silane crosslinkers. The crosslinking reaction activated by moisture is a condensation reaction between the amino groups of the crosslinkers and the hydroxyl end groups of the

PDMS prepolymer. PDMS-B is a mixture of PDMS prepolymer containing vinyl groups, silicon hydride crosslinkers, and a platinum catalyst. Upon heating (190°C), silicon hydride crosslinkers react with the vinyl groups of the PDMS prepolymer as shown in eq. (1). The reaction is similar to that for a two package RTV (room temperature vulcanizing) silicone rubber.⁸



Instrumentation

The thickness of the uniform films obtained by spin coating and by plasma polymerization was measured using a Rudolph Auto EL III ellipsometer. The thickness profile of the sprayed samples was measured using a Sloan Technology Model Dektak IIA profilometer. The optical micrographs and scanning electron micrographs were obtained using a Leitz Orthoplan optical microscope and a Phillips Model 500 scanning electron microscope, respectively. The scratch resistance of the coatings was measured using a Teledyne Taber Model 502 shear/scratch tester. The contact angles of various liquids on the sample surfaces were measured at 20°C, using a Kernco Model GI goniometer. The frictional coefficients between the coatings and 20-lb bond paper were measured using an Instron. The reported values of the scratch resistance, contact angles, and coefficients of friction are the averages of the measurements of five samples. Each sample was measured three times.

RESULTS AND DISCUSSIONS

Surface Topology/Film Thickness

Observations of the spin-coated polydimethylsiloxanes (both A and B) with optical and scanning electron microscopes reveal smooth, featureless surfaces. In contrast, the films prepared by spray coating have rough, nonuniform surfaces [see Figs. 1(a) and 2]. When a rapidly evaporating solvent and a dilute polymer solution are employed in the process, this result is to be expected. Discrete microdroplets of coating solution land on the wafer at different times, resulting in different times of solvent evaporation for some of the droplets. This produces a rugged, nonuniform surface topograph.

In the spin-coating process (3000 rpm), a continuous liquid film radially spreads from the center toward the edge of the wafer within seconds. This allows the solvent molecules on the entire wafer to evaporate in about the same time, resulting in a thin, uniform, continuous, and smooth film.

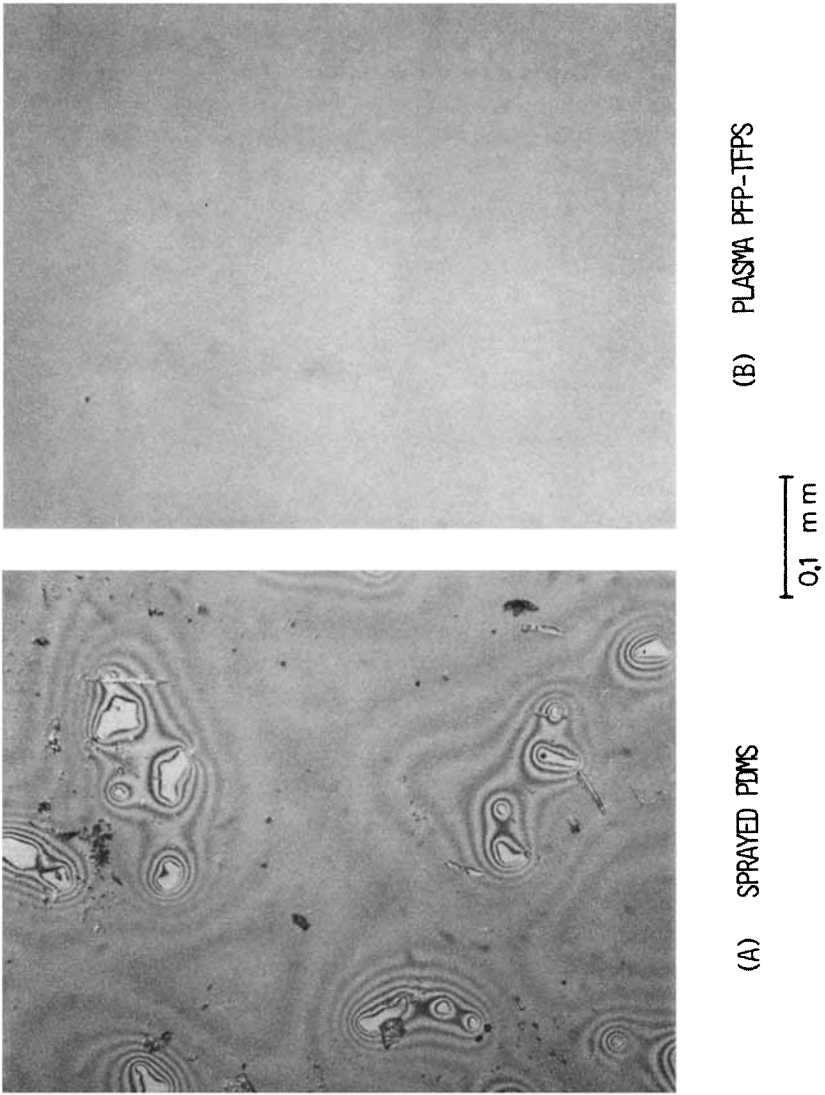


Fig. 1. Optical micrographs of organic thin films coated on silicon wafers.

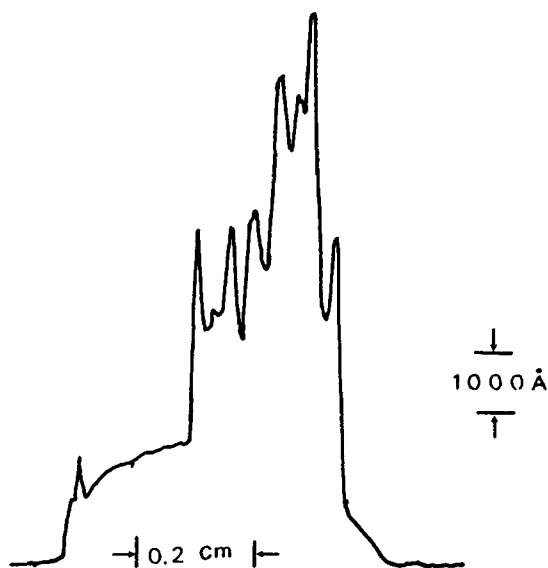


Fig. 2. Thickness profile of the spray-coated PDMS obtained with a profilometer.

The surface of the plasma-polymerized PFP/TFPS copolymer is smooth and uniform [see Fig. 1(b)].

The spin-coated polydimethylsiloxane films are not only uniform, but also extremely thin. The thicknesses of the spin-coated PDMS films, determined by ellipsometry, range from 35 to 50 Å. The thickness of the spray-coated PDMS depends on coating conditions, e.g., speed of the spray and number of passes. Figure 2 illustrates a typical thickness profile of the spray-coated PDMS film, which varies from 2200 to 8000 Å within a wafer.

The thicknesses of plasma-polymerized PFP/TFPS films, estimated with an ellipsometer, range from 250 to 300 Å and are uniform within a wafer.

Friction

The dynamic coefficients of friction (μ) of various polymers coated on silicon wafers were measured by sliding bond paper over a polymer-coated silicon wafer with a 1-lb load at a speed of 5 in./min (0.21 cm/s). Paper was chosen as the countersurface because the possibility of occasional contact between paper and the coating in ink jet printer applications. The results are shown in Figure 3; the coefficients of friction for a bare silicon wafer without coating and a commercial polytetrafluoroethylene (PTFE) film are included for comparison.

The figure shows that the spin-coated PDMS-A has a 0.06 coefficient of friction, the lowest value ever reported for the polymer-paper sliding pairs. The value is only one-third of the coefficient of friction (0.21) between PTFE and paper. PTFE has one of the lowest coefficients of friction among synthetic polymers. It is interesting to note that the coefficient of friction of the spray-coated PDMS ($\mu = 0.31$ for B) is much higher than that of the spin-coated PDMS ($\mu = 0.06$ for A and $\mu = 0.11$ for B). This can be explained in terms of surface topology and friction mechanisms. The two major mecha-

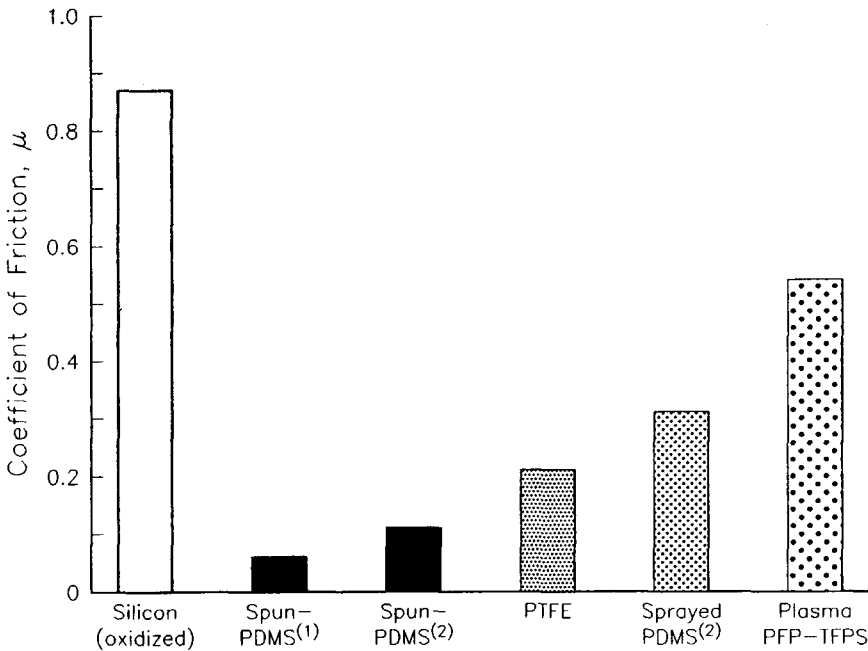


Fig. 3. Dynamic coefficients of friction, μ , for polymer-paper sliding pairs; notes: (1) PDMS-A; (2) PDMS-B.

nisms of sliding friction between a viscoelastic polymer and a harder surface are the deformation of the polymer and the shearing of the adhesive bonds at the interface between two counterfaces.⁹⁻¹¹ Thus, the sliding friction force F can be expressed as follows:

$$F = F_d + F_a$$

where F = sliding friction force, F_d = deformation component, and F_a = adhesive-bond shearing component.

In the deformation mechanism, the frictional force is a function of the dissipation factor of the polymer and load. Deformation loss may involve either hysteresis loss, grooving loss, or both. Hysteresis loss is observed in viscoelastic materials where part of the input energy is dissipated as heat. Grooving loss is observed in materials that are stressed past their yield points, thus causing permanent deformation with the loss of input energy. Friction between the paper and the sprayed PDMS is caused by tearing and cutting, as well as by deformation and adhesion. Bond papers are mixtures of cellulose fibers and inorganic fillers such as clay, calcium carbonate, and titanium dioxide.¹² Its surface abounds with micron-size and submicron-size hard asperities (Fig. 4). These inorganic fillers are hard and abrasive.^{13,14} When the abrasive asperities of the filler come into contact with the rugged texture of the sprayed PDMS, they not only deform the polymer and shear the adhesive bonds but also cut and tear the coating material [Fig. 5(a)]. This accounts for the high friction of the sprayed coating.

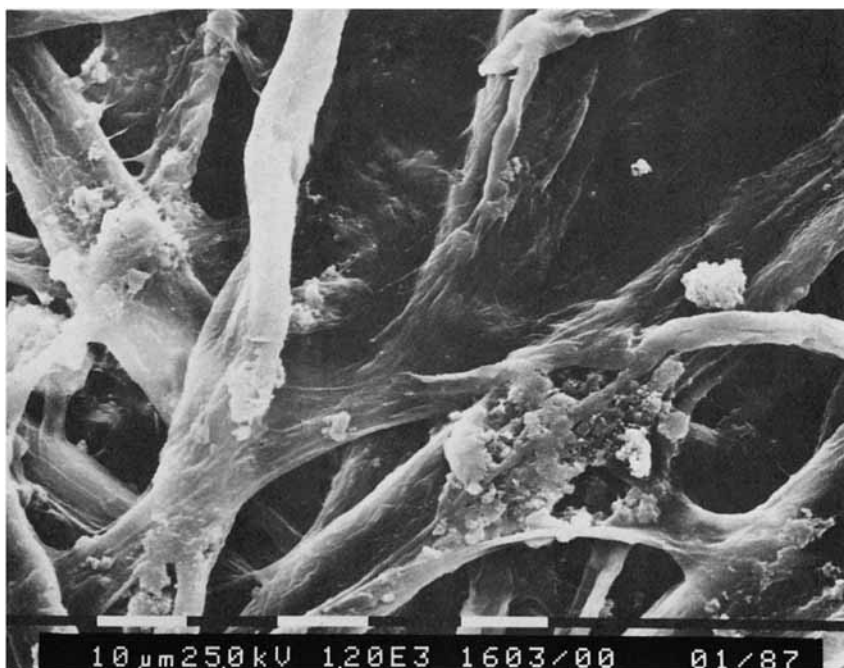


Fig. 4. SEM micrograph of the surface of 20-lb bond paper.

The spin-coated PDMS, on the other hand, is a monolayerlike coating with a smooth surface. For such a smooth, ultrathin film, supported by a smooth and hard silicon substrate, the plowing or deformation process hardly exists. The adhesion mechanism becomes the dominant contributing factor to the friction. The friction force, in this particular case, is affected by the true contact areas and by the molecular interactions at the contact areas. The molecular interactions generally decrease with the decreasing surface energy of the polymer film.

The spin-coated PDMS has low surface energies (20.5 dyn/cm for A, discussed in a later section). Furthermore, the true contact areas between the film and the sliding paper are small. The ultrathin film shares the hardness and rigidity of the silicon substrate. Therefore, the true contact areas are determined by the sizes of the tips of the filler asperities, the sizes and the viscoelastic properties of the cellulose fibers, and the load. Because both the true contact areas and the surface energy are small, the film displays an exceptionally low friction. The μ value of the film is close to those observed with boundary lubricants. The film is an effective durable lubricant for the silicon substrate. It does not wear away by continually sliding against another surface, as do the amphipathic organic molecules, e.g., stearic acid and oleamide.⁹

The difference between the friction of the spin-coated PDMS-A and that of the spin-coated PDMS-B can be partially attributed to the difference in the surface energy between these two films. Using two different coating techniques (spin and spray) to obtain two different types of film from a PDMS allows separate calculation of the adhesion component for the sliding friction.

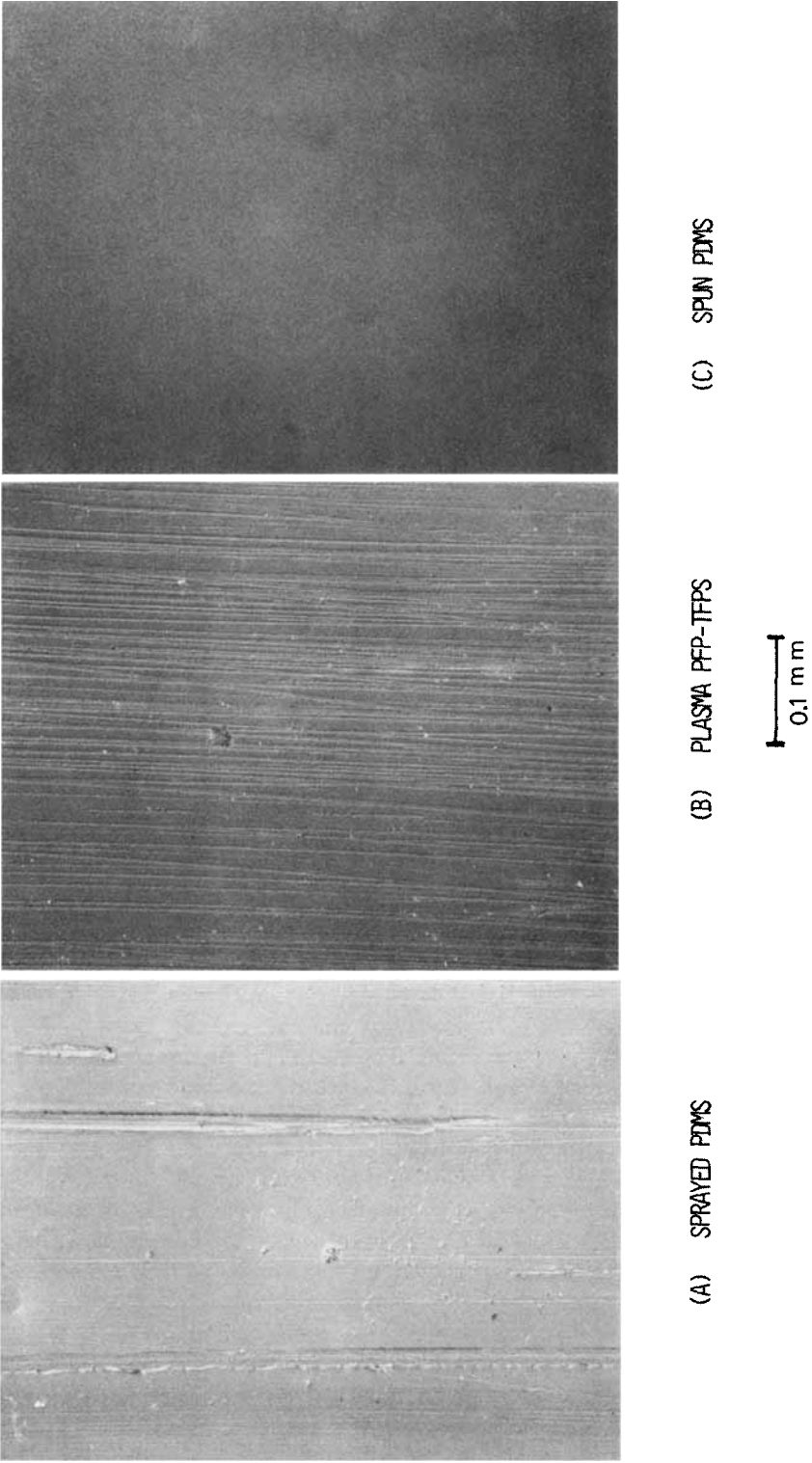


Fig. 5. Optical micrographs of polymer surfaces after the polymer-paper friction test.

For example, the data indicates that approximately 35% of the friction of the sprayed PDMS-B is contributed by the adhesion component, whereas the remainder is contributed by deformation loss and tearing. The sliding friction force for the PDMS films being studied can be written as follows:

$$\text{for spin-coated film, } F = F_a$$

$$\text{for spray-coated film, } F = F_a + F_d + F_t$$

where F_t = force required to tear the polymer by hard asperities.

The plasma-polymerized PFP-TFPS film was expected to exhibit low friction because of its low surface energy (20.0 dyn/cm) and smooth-appearing surface. Contrary to expectation, it exhibits a high friction ($\mu = 0.54$). The reason for the greater friction is that the hard asperities on the sliding paper scratched the polymer coating by a micromachining as illustrated in Figure 5(b). Either the polymer film may have microroughness, which could not be readily observed without using a high-resolution transmission electron microscope, or it lacks a smooth molecular profile. Briscoe, Pooley, and Tabor attributed the abnormally low friction exhibited by a PTFE and a high-density polyethylene to the smooth molecular profile of the polymers.^{15,16} The spin-coated polydimethylsiloxanes have not shown any scratches [Fig. 5(c)] after the frictional tests, suggesting that the surface is much smoother than the plasma-polymerized organic film.

Scratch Resistance and Adhesion

The scratch resistance of the coatings was quantitatively measured by sliding a stainless steel stylus (0.8 mm radius hemisphere) with a vertical load over the film surface. The stylus load was gradually increased until scratches were visible. The critical load at which a continuous scratch line longer than 0.5 cm was formed is taken as a measure of failure of scratch resistance. The adhesion of the coatings to the silicon substrate was semiquantitatively evaluated after the scratch tests by examining the wear tracks for film detachment, using an optical microscope. The test results are shown in Table I.

TABLE I
Scratch Resistance, Adhesion, and Thickness of Polymer Films

| Type of film | Scratch resistance (g) | Adhesion (g) | Thickness (Å) |
|-------------------------|---|----------------------------|------------------|
| PFP-TFPS Plasma film | < 50 | Delaminate at 700 | 250-300 |
| Sprayed PDMS-B | 70-270 | Delaminate at 70-270 | 2200-21,000 |
| Spun PDMS-A & B | > 1000 ($> 3.6 \times 10^{10}$ dyn/cm ²) ^a | No delamination at 1000 | 35-50 |

^aThe minimum pressure is estimated based on the load and the scratched area on the PFP-TFPS film.

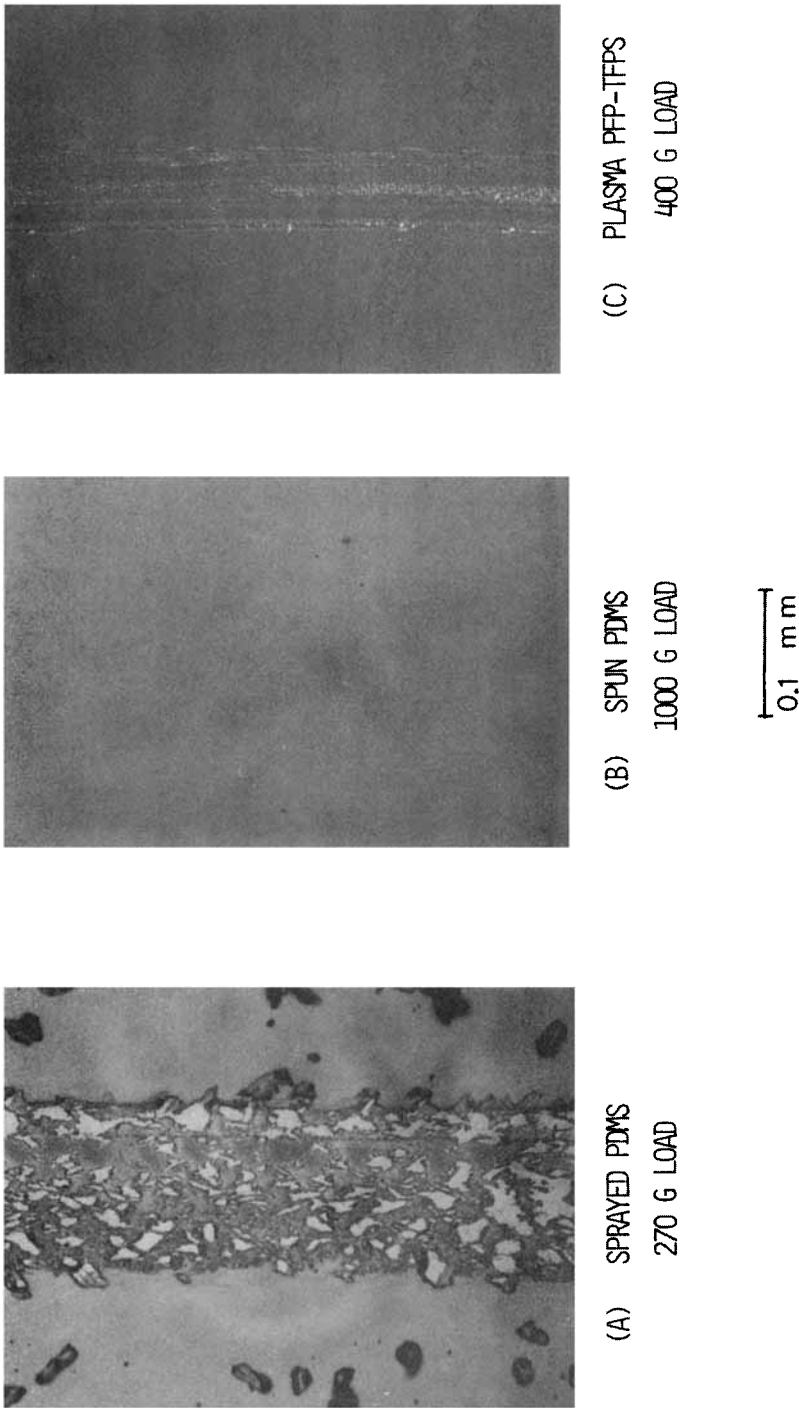


Fig. 6. Optical micrographs of the polymer surfaces after scratching tests using a stainless steel probe (0.8 mm radius).



Fig. 7. SEM micrograph of scratches formed by a stainless steel probe (0.8 mm radius) on the spray-coated PDMS.

The data indicate that the spray-coated PDMS-B has a weak scratch resistance (ranging from 70 to 270 g, depending on samples). This result was expected, because the scratching mechanism or the abrasive wear process for a rough-surface polymer film is similar to the frictional mechanisms discussed previously. It involves deformation, shearing of adhesion bonds, microtearing, and microcutting.¹⁷⁻¹⁹ Figures 6(a) and 7 show the micrographs of scratches formed by a stainless steel probe on the spray-coated silicone film. Film detachments exist in some of the areas, indicating poor adhesion of the coating to the substrate. By contrast, the spin-coated polydimethylsiloxanes (A and B) show neither film delamination nor scratches by the stainless steel probe under the maximum load (1000 g) available for the tester [Fig. 6(b)]. Thus, the spin-coated polydimethylsiloxane films display unusually high scratch resistance and very strong adhesion to the substrate. These results are expected because it has an exceptionally low friction, smooth surface, low surface energy, and hardness imparted by a silicon substrate.

For PDMS-A, some hydroxyl groups present on the silicon dioxide surface could react with the amino groups attached to the polymer to form

Si—O—Si covalent bonds at the polymer-silicon interface. This reaction would promote stronger adhesion of the polymer to the silicon substrate.

The high wear-resistance property is particularly useful when applied to the coating for an ink jet nozzle plate. The coating must withstand sliding actions by abrasive paper debris during functional performance or machine maintenance. Plasma-polymerized PFP-TFPS film has a weak scratch resistance (less than 50 g) and moderate adhesion to a silicon substrate. Examination of the scratches on the PFP-TFPS surface, produced by a stylus under a 400-g load, revealed that the top layer of the film was pushed aside by the moving probe, but a thin layer of the film was still attached to the substrate [Fig. 6(c)]. It is likely that the residual layer is TFPS that was deposited on the silicon wafer prior to introducing PFP monomer as an adhesion promoter. TFPS homopolymer is harder than PFP homopolymer. The cohesive failure might have occurred in the PFP-TFPS copolymer layer in the middle or in the PFP layer on the top of the film. The adhesive failure did occur when the load was increased to 700 g.

Surface Tension and Wettability

The wettability of the polymer coatings was evaluated by determining the critical surface tension (γ_c) and the ink-sheeting time. The ink-sheeting time was measured by immersing a polymer film (coated on a 1.5-in. diameter silicon wafer) into an ink at room temperature and then by lifting the wafer vertically off the liquid surface. The time interval between when the wafer is lifted and when the last drop of liquid runs off the wafer is defined as the ink-sheeting time.

The critical surface tension was determined by using the Zisman method.²⁰ The γ_c values of the polymer coatings, the contact angles (θ) of water on the coatings, and the results of the ink-sheeting time measurements are listed in Table II. The data show that the plasma-polymerized PFP-TFPS film and the spin-coated PDMS-A yield γ_c values of 20.0 and 20.5 dyn/cm, respectively. The values are close to those for PTFE²¹ and the polydimethylsiloxane coatings for pressure-sensitive adhesive release applications.²² The low values of the surface tension of these two films suggest that both surfaces are hydrophobic. The water repellent property of both films is further supported by their low polarity (1.5%) as determined by the two-liquid method proposed

TABLE II
Surface Tension and Ink Wettability of Polymer Film

| Type of film | θ (deg) (H ₂ O) | γ_c (dyn/cm), 20°C | Ink-sheeting time ^a (s) |
|---------------------|---|---------------------------------|---------------------------------------|
| Spin-coated PDMS-A | 114 | 20.5 | 2.4-3.0 |
| Spin-coated PDMS-B | 111 | 23.3 | — |
| Spray-coated PDMS-B | 116 | — ^b | 3.4-8.0 |
| Plasma PFP-TFPS | 114 | 20.0 | 2.0-6.0 |

^aA propylene glycol based ink was used to measure the ink-sheeting time. The values are the ranges of 10 samples.

^b γ_c is not determined because of surface roughness.

by Wu.²³ The surface tension of the spin-coated PDMS-B was found to be 23.3 dyn/cm. Note that the contact angle of water on the sprayed PDMS-B is 5° higher than that on the spun PDMS-B because the sprayed PDMS has a rough surface whereas the spun PDMS has a smooth surface. A rough surface has a greater surface area than a smooth surface within a given geometrical area. The ratio of actual surface area to geometrical surface area is the roughness factor, introduced by Wenzel to correct the surface energy change caused by surface roughness.^{24,25} The roughness factor is also defined by the ratio of the cosine of the apparent contact angle to the cosine of the true contact angle. For a rough surface, if the true contact angle is greater than 90°, the apparent contact angle is greater than the true contact angle. If the surface of the spin-coated PDMS represents an ideal smooth surface, then the roughness factor of the sprayed PDMS would be 1.2.

The spin-coated PDMS-A exhibits a shorter and more consistent ink-sheeting time (2.4–3.0 s) than the PFP-TFPS film (2.0–6.0 s) or the sprayed PDMS-B (3.4–8.0 s). The ink-sheeting time correlates with the ink wettability of the nozzle-plate coating during a printing process better than the contact angle does. The wettability of the nozzle-plate coating decreases as ink-sheeting time decreases. A low wettability is desirable for an application to the ink jet nozzle plate. It appears that ink wettability is closely related to the hysteresis effect. A hysteresis effect is observed when the advancing and receding contact angles are different. It could be caused by a rough surface, by contamination of either the solid surface or the liquid, or by surface immobility.²⁶ For the ink jet application, the hysteresis could be serious. First, the ink is not a pure liquid; in a sense, the liquid is contaminated. Second, the solid surface could be contaminated during the printing process by the additives in the ink. Third, if the ink contains a surfactant, there will be surface immobility. To obtain low ink wettability of the nozzle plate, the hysteresis effect must be minimized.

Solubility and Stability

All of the PDMS and the PFP-TFPS film are insoluble in water and common organic solvents such as ethanol, acetone, ethyl acetate, tetrahydrofuran, ethylene glycol, and hexane. This fact suggests that these films are highly crosslinked. The long-term stability of the coatings in various environments, especially water and glycol (common solvents for inks), has been investigated. After exposure to a given environment, the coatings were evaluated in terms of contact angle, scratch resistance, and adhesion. None of the PDMS coatings showed even a slight degradation after exposure to a hot and humid environment (35°C and 90% relative humidity) for 1 month. The condition simulates an extreme office environment in which an ink jet printer may be installed and operated. Table III shows the soaking effects of water and propylene glycol upon the contact angles. Table IV shows the soaking effects of water and propylene glycol upon scratch resistance.

The data shows that the PDMS-A is stable after soaking in either water or propylene glycol, as evidenced by its constant contact angle and scratch resistance as well as by its retention of strong adhesion to the substrate. The contact angles of ethylene glycol on the spray-coated PDMS-B decreased by

TABLE III
Soaking Effects of Water and Propylene Glycol on Contact Angles

| Type of film | Initial contact angle, EG ^a (deg) | Final contact angle, EG ^a (deg) | |
|-------------------|--|--|-------------------------------------|
| | | Water-soaked, 2 weeks | PG ^a -soaked, 2 weeks |
| PDMS-A (spun) | 92 | 92 ^b | 92 ^b |
| PDMS-B (spun) | 91 | 84 ^b | 87 ^b |
| PDMS-B (sprayed) | 94 | 90 ^c | 94 ^c |
| PFP-TFPS (plasma) | 90 | 44 ^c | 78 ^c |

^aEG = ethylene glycol; PG = propylene glycol.

^bSoaked at 45°C.

^cSoaked at 60°C.

TABLE IV
Soaking Effects of Water and Propylene Glycol on Scratch Resistance

| Type of film | Decrease in scratch resistance (%) | |
|------------------|------------------------------------|------------------------------|
| | Water, 2 weeks | Propylene glycol, 2 weeks |
| PDMS-A (spun) | None ^a | None ^a |
| PDMS-B (spun) | None ^a | None ^a |
| PDMS-B (sprayed) | 27% ^b | None ^b |

^aSoaked at 45°C.

^bSoaked at 60°C.

4% to 7.7% after soaking in water at 45°C for 2 weeks. Soaking the spin-coated PDMS-B in propylene glycol produced a similar effect. However, the scratch resistance of the PDMS-B, regardless of the coating process, is not affected by propylene glycol. The scratch resistance of the sprayed PDMS-B decreased by 27% after soaking in water at 60°C for 2 weeks.

The most pronounced effect of the soaking test was observed on the plasma-polymerized PFP-TFPS film. The contact angles of ethylene glycol on this film decreased by 46 and 12%, respectively, after soaking in water and propylene glycol for 2 weeks. The change in surface energy for the plasma-polymerized film and the methods used to stabilize or to reduce the surface energy of the film will be discussed in a separate paper by the author.

CONCLUSIONS

A smooth, ultrathin film of PDMS spin-coated on silicon displays the properties of high scratch resistance, low friction, low surface energy, and strong adhesion. The film is stable in water, propylene glycol, and hot and humid environments. The thin film is an effective and durable solid lubricant. It can be widely used as a protective coating for many critical components of computers, printers, copiers, and other products.

Spray coating of PDMS yields a nonuniform, rough film with low scratch resistance, high friction, low surface energy, and weak adhesion. The plasma-polymerized PFP-TFPS film exhibits the physical properties of low scratch resistance, high friction, low surface energy, and medium adhesion. The surface energy of this film increases with time upon soaking in water and propylene glycol.

A spin-coated PDMS thin film gives a 0.06 dynamic coefficient of friction against a paper, the lowest value ever reported for the polymer-paper sliding pairs. This value is close to those observed with boundary lubricants. The exceptionally low friction and unusually high scratch resistance of the spin-coated PDMS are attributed to the absence of deformation and tearing components and a low adhesion component in the sliding friction mechanism.

The spin-coating process allows using even a soft polymer (bulk property), because the resulting thin film exhibits friction and scratch resistance that are drastically different from those of the bulk.

The following characteristics are important to obtaining a protective film with high scratch resistance, low friction, and strong adhesion:

1. The film is ultrathin, uniform, and smooth.
2. The substrate is smooth and hard.
3. The film has a low surface energy.
4. A strong affinity exists between the film and the substrate.

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