Microstructure Formation on Polytetrafluoroethylene (PTFE) and Perfluoroalkoxy (PFA) Bulk Plates by a Magnetron Enhanced Reactive Ion Etching System

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The etching characteristics of polytetrafluoroethylene (PTFE) and perfluoroalkoxy (PFA) bulk plates were studied in a magnetron enhanced reactive ion etching (M-RIE) system. The etch rates of the plates for oxygen plasma were investigated under the pressure range 0.1–2.0 Pa, and were found to strongly correlate with the self-bias voltage. The plates presented smooth surface in the 0.1–1.0 Pa pressure range, and rough surfaces at 1.5 Pa and 2.0 Pa. The roughness was introduced by a micromask sputtered from the chamber material. The titanium etching mask exhibited lower etch rates for oxygen plasma than aluminum and silicon dioxide. Finally, using the dry-etched titanium mask in low-pressure oxygen plasma, we fabricated a 5-μm pitch line-and-space structure on a PTFE plate and a 4-μm square pillar array on a PFA plate.

1. Introduction

Fluorine polymer exhibits various desirable properties, such as strong chemical resistance and high hydrophobicity. Therefore, fluorine polymer microfabrication has been extensively investigated, and a low-cost technique for fabricating bulk plates of fluorine polymer is strongly expected. Lithography, electroplating and molding processes (LIGA) have achieved high etch rates through the hole-etching of polytetrafluoroethylene (PTFE) film, but lack versatility because of their high initial investment and operating cost1). Another technique is the fabrication of microchannels on perfluoroalkoxy (PFA) plates by the hot embossing process2). However, conventional RIE systems can readily form such microstructures by orienting the high energy ions under low pressure conditions, the impact of ions extracted from plasma on the grid material frequently generates micromasks. Moreover, to uniformly etch a large area, the tilt angle of the substrate must be optimized for the particular etching micropattern. Lee et al.4) barely mentioned the surface roughness, but whether they achieved a smoothed etched surface by their instrument configuration is doubtful, as researchers adopting similar configurations reported rough etched surfaces5).

Reactive ion etching (RIE) is a fundamental technique in semiconductor manufacturing, and has conventionally fabricated semiconductor materials such as silicon and silicon dioxide. However, the formation of microstructures on bulk plates of fluorine plastic have been limited to foils or thin films deposited on substrates6,7). The main reasons for these limitations appear to be thermal deformation and high roughness of the etched surface. Conventional RIE fabricates semiconductor materials with higher thermal resistance, and is not designed for polymer materials. Therefore, polymer etching by RIE is vulnerable to deformation and warpage. Moreover, polymer surfaces etched by RIE are rougher than the untreated surface, precluding the use of RIE in various applications of polymer materials, such as precise plastic molds, microfluidics and microcomponents8–11).

Previously, we micro-fabricated bulk plates of polymethylmethacrylate (PMMA) with lower heat resistance than fluorine polymer. For this purpose, we developed an RIE system with an original electron cyclotron resonance plasma source12), and a micropillar array structure with a gap aspect ratio of 10, which maintained a smooth surface. We then demonstrated the filtration microfluidics and size separation of microparticles in the fabricated bulk plates.

In this study, we develop a practical magnetron-enhanced RIE (M-RIE) system that etches bulk polymer plates of PTFE and PFA. Among the fluorine polymers, PTFE is lauded for its high hydrophobicity and chemical
resistance. PFA not only exhibits similar properties to PTFE, but also possesses a unique thermoplastic property. Our system employs a sample stage with high thermal conductivity that avoids thermal deformation, and a high speed pumping mechanism that prevents micro-mask deposition. The etching was performed in pure oxygen plasma, and the etch rates, surface morphologies and atomic compositions of the PTFE and PFA plates were studied as functions of the chamber pressure. To demonstrate the usefulness of the proposed etching method, we fabricated 5-μm pitch line-and-space structure on a PTFE plate and a 4-μm square pillar array on a PFA plate.

2. Experimental

2.1 Etching Sample

The etching samples were PTFE (PTFE-M, Daikin Industries Ltd., Osaka, Japan) and PFA (NEOFLONG, Daikin Industries Ltd., Osaka) plates of thickness 1 mm cut into 25 × 25 mm² squares. The arithmetic mean surface roughness (Ra) values of PTFE and PFA were approximately 200 nm and 80 nm, respectively. The samples were ultrasonically cleaned with deionized water and absolute ethanol before the etching process.

2.2 Etching System

The RIE of the fluorine polymer plates was carried out in our original M-RIE system, designed for polymer plate etching. Figure 1 is a schematic of the RIE system. The inner diameter of the vacuum chamber was 150 mm, and the distance between the quartz cover plate and sample stage was 30 mm. Permanent magnets installed on the quartz cover plate create a confined magnetic field above the sample, generating a high density plasma under low pressure conditions for anisotropic, high-speed etching. The magnets are circularly arranged with successive opposite polarities. The sample stage (diameter 82 mm) has a low thermal capacity, enabling efficient cooling of samples, and the coolant channel is located 10 mm from the sample to obtain high thermal conductivity. The coolant is insulated to avoid radio frequency (RF) power leakage from the sample holder to other stage components. The distance between the quartz cover plate and the sample was optimized to prevent deformation after a 60-minute RIE application at an RF power of 50 W. The ultimate pressure in the chamber is 3.0 × 10⁻³ Pa or less. The conductance valve adjusts the pressure increase by gases emitted during etching.

2.3 Etching Conditions

All of the etching procedures were carried out at an RF power of 50 W and a stage temperature of 273 K. The etching gas was pure oxygen gas with a flow rate of 10 cm³/min. Conventional polymer etching uses fluorine with gas species such as CF₄, SF₆ and C₂F₆. These gases were not used in the present study, because they constitute specific etching agents for titanium, aluminum and silicon dioxide, which are predetermined etching mask materials.

2.4 Dependency of Etch Rates on Chamber Pressure

The PTFE and PFA plates were attached to (2 × 10)mm² pieces of adhesive polyimide tapes, and centrally placed in an aluminum (A5052) sample holder with a diameter and thickness of 80 mm and 3 mm, respectively. The holder was mechanically fixed onto the sample stage with four bolts. The polyimide tapes provided the masking for the etched PTFE and PFA plates. The etching was carried out over a range of pressures (0.1–2.0 Pa). After the etching, the polyimide tapes were peeled off and the etch steps were measured by a surface roughness measurement instrument (Form TalySurf PGI 1200, Taylor Hobson, USA). The etch steps were then used in the etch rate calculations. At each pressure, the self-bias voltage was recorded using a digital oscilloscope and the relationship between the voltage and etch rate was determined.

2.5 Dependency of Surface Morphology on Chamber Pressure

The surface morphologies and elemental analyses of the samples prepared in subsection 2.4 were investigated using a field emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) system (JSM-7001F, JEOL Ltd., Tokyo, EDAX Genesis, Ametec Inc., USA). In particular, to determine the correlativity between the surface element distribution and surface morphology, we obtained two-dimensional elemental images of the etched PTFE sample at 2.0 Pa. The surface roughness (Ra) of each etched surface was also measured by the abovementioned roughness measurement instrument.

2.6 Dry Etching Resistance of Ti, Al, SiO₂ on PTFE

The dry etching resistance of titanium (Ti), aluminum (Al) and silicon dioxide (SiO₂) thin film on the PTFE plates was also discussed. Ti and Al thin films were formed by the vacuum deposition method to thicknesses of 120 nm and 90 nm, respectively. SiO₂ thin film was electron beam evaporated to a thickness of 110 nm. Two (2 × 10)mm² areas were masked on each film by polyimide tape, leaving two non-deposited areas for determining the degree of removal. The etch rates of Ti and Al were calculated by dividing the film thickness by the time required to remove approximately 80% of the total deposited area. The SiO₂ etch rate was calculated by dividing the film thickness by the time at which the sample surface on the dismounted holder in the vacuum chamber showed a hydrophilic property.

2.7 PTFE and PFA Microstructure Formation

PTFE and PFA microstructures were formed by ap-
plying a 120 nm-thick Ti film as an etching mask. Positive photoresist (AZP1350, AZ Electronic Materials, USA) was spin coated on the plates at a thickness of 0.5 μm, and the resist was patterned by the conventional photolithography process. A line-and-space pattern and square pillar array patterns of pitch 5 μm, 10 μm, 20 μm, 30 μm, 50 μm, 100 μm, and 200 μm were formed on the Ti film. The RIE was performed in two steps. In the first step, the exposed Ti film was dry-etched using CF₄ plasma. The etching was carried out at a chamber pressure of 0.1 Pa, an RF power of 50 W, a stage temperature of 273 K, and an etching duration of 8 minutes. Here we applied the dry etching process because when Ti is removed by the wet etching process, the low surface energy of the fluorine polymer causes film peeling in the acid solution. In the second step, the PTFE and PFA plates were dry-etched using pure oxygen plasma. Apart from the plasma gas and etching duration, the etching conditions were unchanged from the first step. To obtain the desired surface roughness of the etching and the directional nature of the incident ion flux, we set the chamber pressure to 0.1 Pa. The etching durations of PTFE and PFA were 25 and 30 minutes, respectively. The etched shapes were evaluated by SEM observation.

3. Results and Discussion

3.1 Dependency of Etch Rates on Chamber Pressure

Figure 2 shows the pressure dependencies of the PTFE and PFA etch rates. The horizontal etch depth uniformity was less than 5% absolute across the sample surface. Both etch rates increased with increasing pressure. The etch rates of PTFE and PFA were maximized at 1.5 Pa (780 nm/min) and 2.0 Pa (730 nm/min), respectively. The etch rates of PTFE were higher than those of PFA over the entire range of pressure. PTFE has higher fluorine content than PFA. Therefore, the amount of etched fluorine acting as the etching agent is thought to relate to the difference of the etch rate between PTFE and PFA.

The etch rates were also proportional to the self-bias voltage (see Fig. 3). These results support that the radical sites generated by the ion bombardment initiate the etching process, as hypothesized in Berenschot et al. Although the initial etching step in hydrocarbon polymer such as PMMA and polyethylene is dominated by free radical addition or hydrogen extractive reactions, ion bombardment plays an important role in PTFE and PFA etching. In addition, the etch rates may be influenced by the plasma density, which seems to increase with increasing pressure.

3.2 Dependency of Surface Morphology on Chamber Pressure

Figure 4 shows SEM photographs of the etched PTFE surfaces under each chamber pressure condition. The top left section of each photograph is the area masked by the polyimide tape, and the central part is the etched surface area. Chamber pressures from 0.1 Pa to 1.0 Pa, yielded smooth surfaces, whereas the surfaces formed at 1.5 Pa and 2.0 Pa exhibit a “grassy” appearance. At 2.0 Pa, the diameters and heights of the grassy structures were 0.5–1.0 μm and 0.5–0.8 μm, respectively. The etched surfaces of PFA displayed the same tendency.

Figure 5 shows the atomic concentrations of the etched PTFE and PFA surfaces obtained by EDS. In both PTFE and PFA, the concentrations of four elements exhibit similar changes with increasing chamber pressure. The fluorine concentrations were almost constant at pressures below 1.0 Pa, and increased over 1.5 Pa. In the low pressure range, the fluorine is thought to be intensively desorbed, relative to the untreated surfaces. At 1.5 Pa and 2.0 Pa, the desorbed fluorine was probably redeposited on the lateral face of the grass. The carbon concentrations demonstrated the opposite trend; namely, they increased below 1.0 Pa and decreased above 1.5 Pa. The absence of surface fluorine probably accounted for the former, whereas the additional redeposited fluorine probably reduced the carbon concentration at higher pressures. The oxygen concentration remained almost stable under all pressure conditions. On the other hand, the aluminum concentrations were considerably higher at 1.5 and 2.0 Pa than at lower pressures and on the untreated surface. It appears that aluminum sputtered on the holder or chamber was redeposited on the
PTFE or PFA surfaces by backscattering. The probability of backscattering is increased at higher pressures because the mean free paths of oxygen molecules at 1.5 and 2.0 Pa (7 mm and 5 mm, respectively) are much shorter than the chamber diameter. This redeposited aluminum acts as a micromask, forming grass-like surfaces on the PTFE and PFA plates.

Figure 6 shows the aluminum elemental image mapping of the etched PTFE surface at 2.0 Pa. The grass positions were generally located at aluminum detection positions. These results support that grassy surface resulted from aluminum micromasking.

Figure 7 shows the surface roughnesses (Ras) of the etched PTFE and PFA surfaces under each pressure condition. Although the measured data do not directly reflect the grass shapes, they reveal the surface morphologies. In the lower pressure range (0.1–1.0 Pa), the PTFE and PFA surfaces were as smooth as the untreated surfaces. At 1.5 and 2.0 Pa, the PTFE and PFA surfaces were roughened by the grass formations caused by the aluminum micromask shown in Fig. 5. At 1.5 Pa, the measured Ras of PTFE and PFA were approximately 280 nm and 110 nm, respectively. In the high pressure range, the PTFE surfaces became rougher than the PFA surfaces. The aluminum micromask deposited on the roughened surface with dimples or grooves was poorly etched. Therefore, a remarkable roughness change of PTFE over 1.5 Pa is likely to reflect the different roughnesses of the original untreated PTFE and PFA surfaces.
3.3 Dry Etching Resistances of Ti, Al and SiO$_2$ Film on PTFE

Figure 8 shows the etch rates of the Ti, Al and SiO$_2$ films on PTFE bulk plate as functions of pressure from 0.1 to 2.0 Pa. The etch rates of Ti and Al gradually increased with increasing pressure. Given that these etch rates were also proportional to the self-bias voltage (see Fig. 2), we suggest that physical etching dominated the etching mechanism. The etch rates of SiO$_2$ film also increased with increasing pressure, and exceeded the etch rates of Ti and Al over the entire pressure range. It is expected that the etched fluorine combined with silicon in the film, forming volatile products such as SiF$_4$.

3.4 PTFE and PFA Microstructure Formation

Figure 9 shows SEM photographs of the microstructures on the PTFE and PFA plates. A line-and-space pattern with a pitch of 5 $\mu$m was obtained on the PTFE plate. Each step was 4 $\mu$m wide and 10 $\mu$m high, giving an aspect ratio of 2.5. An array of micro-pillars appeared on the PFA plate. The pillars measured 4 $\mu$m $\times$ 4 $\mu$m $\times$ 12 $\mu$m and their aspect ratio was 3.0. The side wall angles of both microstructures were almost 90°.
4. Conclusion

In this paper, we investigated the mechanism by which the surface morphology forms on PTFE and PFA bulk plates during oxygen plasma etching. In addition, we formed microstructures with high aspect ratios on PTFE and PFA bulk plates under smooth surface etching conditions. At present, the preferred coating on Si or glass microstructures is fluorine resin, which exhibits superior properties. However, a uniform coating of fluorine resin on microstructures is difficult to achieve by spin-coating or dip-coating, and cracking or peeling easily occurs under physical impact or thermal shock stress. Moreover, coating on polymer plates requires cumbersome procedures such as specialized primers or precise heat treatment. These problems can be potentially overcome by our RIE technique, which directly processes the fluorine plate with high precision, high aspect ratio, shape reproducibility, and reutilization ability. The technique presents as a promising tool for microelectromechanical systems (MEMS), micro-reactors, and fluorine microcomponents.

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