Effect of oxygen addition to an argon plasma on etching selectivity of poly (methyl methacrylate) to polystyrene

Makoto Satake
Taku Iwase
Masaru Kurihara
Nobuyuki Negishi
Yasuhiko Tada
Hiroshi Yoshida
Effect of oxygen addition to an argon plasma on etching selectivity of poly(methyl methacrylate) to polystyrene

Makoto Satake
Taku Iwase
Masaru Kurihara
Nobuyuki Negishi
Hitachi, Ltd.
Central Research Laboratory
Kokubunji, Tokyo 185-8601, Japan
E-mail: makoto.satake.bz@hitachi.com

Yasuhiro Tada
Hiroshi Yoshida
Hitachi, Ltd.
Hitachi Research Laboratory
Hitachi, Ibaraki 319-1292, Japan

1 Introduction
Scaling down of semiconductor devices has required continual improvement in photolithography techniques such as immersion lithography and double-patterning lithography. “Directed self-assembly” (DSA), which combines self-assembling materials with lithographically defined pre-patterns, has been widely studied.1–6 According to the International Technology Roadmap for Semiconductors 2012, DSA is a potential candidate as a next-generation lithography technique for 16-nm half-pitch and beyond.7 Two key advantages of DSA are its capability of making a nanoscale structure and its cost effectiveness.

One promising approach for DSA is the use of diblock copolymers, which consist of two chemically different immiscible polymers connected at one end of each polymer chain. During DSA, a diblock copolymer is segregated into two polymer phases on the surface of a substrate in a chemically or morphologically controlled manner.8,9 The morphological structure of a phase-separated diblock copolymer, such as alternating lamellae, hexagonally packed cylinders, and spherical domains in body-centered lattice, depends on the interaction parameters, the molecular weight, and the composition of the two polymer blocks.10,11 Among the variety of diblock copolymers, poly(styrene–block-methyl methacrylate) (PS-b-PMMA) has been extensively studied as a potential candidate for DSA. It has been reported that PS-b-PMMA forms microphase-separated structures smoothly, because the value of glass-transition temperatures of PS and PMMA are close.12

One important issue in the development of DSA with diblock copolymers is to produce high-etching selectivity of PMMA to PS (hereafter “PMMA/PS etching selectivity”). This process is used to fabricate a high-quality PS mask for subsequent etching processes. One standard approach for achieving high PMMA/PS etching selectivity is to use argon–oxygen-based plasmas.13–15 Several other plasma-etching processes have been reported.16–18 In plasma etching, ions and radicals generated in the plasma react with the material on the wafer. In 1983, Gokan et al. researched the reaction of organic polymers with only ions by using either argon or oxygen ion-beam etching (IBE) and showed that the etching rate of organic polymers changes when the carbon and oxygen contents in the polymers are changed.19 They obtained PMMA/PS etching selectivity of around 2.0 in the case of etching with either argon or oxygen ion beams. Recently, Ting et al. compared the PMMA/PS etching selectivities of five different plasmas, namely argon plasma, oxygen plasma, argon-oxygen mixed plasma, tetrafluoromethane plasma, and oxygen-trifluoromethane mixed plasma.13 They reported that the argon-oxygen mixed plasma is the best choice for PMMA etching, because it produces reasonably high PMMA/PS etching selectivity of 2.04 and a smooth PS mask surface. The argon-oxygen mixed plasma is thus regarded as a promising candidate for selective PMMA/PS etching. They also reported that using argon plasmas, which produce the highest etching selectivity of around 7, are accompanied by a visibly roughened surface. However, these reports contain little information on the etching mechanism of PMMA.

Given the above-described background, in this work the underlying mechanism of selective PMMA etching in argon-oxygen-based plasmas (namely inductively coupled plasmas (ICPs) composed of argon gas only, oxygen gas...
only, or an argon-oxygen gas mixture] was clarified. It was
found that the addition of a small amount of oxygen to argon
improves PMMA/PS etching selectivity. A simple model for
the improvement in selectivity (which is consistent with the
observed etching characteristics) is proposed. The argon-
oxygen gas mixture was used to fabricate a high-quality
PS mask from a PS-\textit{b}-PMMA fingerprint pattern.

### 2 Experimental Procedure

Two blanket films, made of PMMA homopolymer (P4078-
MMA) and PS homopolymer (P1758-S) purchased from
Polymer Source Inc., Dorval, Quebec, Canada were used
to evaluate the etching depth of each polymer and PMMA/
PS etching selectivity. Number-average molecular weights
of both PMMA and PS blanket films are 11,500. The two
blanket films were spin coated from toluene solution (2 wt
%) at 1000 rpm on silicon substrates to thicknesses of
100 nm. Three kinds of PS-\textit{b}-PMMA fingerprint patterns
(P8966-SMMA, P8533-SMMA, and P5539-SMMA) pur-
chased from Polymer Source Inc. with target full pitches
of 25.5, 41.0, and 77.0 nm—were also deposited on substrates
as described below, and the patterns were etched to form PS
masks. The number-average molecular weights of PS/PMMA
in each PS-\textit{b}-PMMA pattern were 22,000/22,000 for the
25.5-nm full-pitch pattern, 35,000/33,500 for the 41.0-nm
full-pitch pattern, and 80,000/80,000 for the 77.0-nm full-
pitch pattern. Before forming the PS-\textit{b}-PMMA patterns,
the silicon substrates were cleaned in a 7:3 mixture of sulfuric
acid and hydrogen peroxide (piranha solution) at 80°C for
10 min and rinsed with deionized water. Hydroxyl-terminated
silicon substrates were cleaned in a 7:3 mixture of sulfuric
toluene to remove any unreacted polymers, and PS-
\textit{r}-PMMA fingerprint patterns were formed on the substrates.
PMMA brush and annealed at 230°C for 6 h. Then, PS-
\textit{r}-PMMA fingerprint patterns were formed on the substrates.
The blanket films and fingerprint patterns were etched in an
ICP etching system for 300-nm wafers, in which a two-
turn coil, connected to a 13.56-MHz source power, was
located above an Al\textsubscript{2}O\textsubscript{3} dome. A faraday shield covering
the dome is connected to a source-power line. The energy
of incident ions into the internal surface of the dome is
adjusted by changing the voltage of the faraday shield
(FSV). The detail of the equipment is described elsewhere.
The source power was varied from 100 to 1000 W, and FSV
was 50 or 400 V. An optical emission spectroscopy apparatus
was installed in the view port on one side of the chamber
wall. The bottom electrode of the ICP system was connected
to an 800-kHz bias power supply to control the energy of
ions. The bias power ranges from 0 to 10 W. Argon, oxygen,
and an argon-oxygen mixture were used as discharge gases.
Process pressure was controlled by using a variable-conduct-
ance gate valve. The process pressure was varied from 0.5
to 2.0 Pa. In the argon plasma, the main etching mechanism
is physical sputtering by argon-ion bombardment. However, it
is expected that a small amount of oxygen radicals enhances
the etching rates of polymers, because the Al\textsubscript{2}O\textsubscript{3} dome is
also bombarded by argon ions and oxygen impurities
(which originate from the dome) and are mixed into the
argon plasmas.

IBE with argon ions was used to evaluate the etching rate
of PMMA. When IBE is used, the etching-rate change due to
oxygen incorporation is avoided, because the PMMA is
etched only by ions when the PMMA and the plasma
(i.e., ion source) are separated. Therefore, hardly any oxygen
radicals arrive at the surface of the PMMA even when a small
amount of oxygen radicals is produced in the ion source.

Etching depth was measured by stylus profilometer
(Tencor P-11) at 20-μm/s scan speed, 50-Hz sampling
rate, and 5-mg stylus force. The etching depth was measured
five times for each sample. The etching depth was estimated
by averaging the five etching-depth data. The compositional
change in the surface of the PMMA during argon-ion etching
was evaluated by x-ray photoelectron spectroscopy (XPS)
equipped with an argon-ion gun (Theta Probe manufactured
by Thermo Fisher Scientific, East Grinstead, West Sussex,
UK). The XPS analysis, with spatial resolution of 400 μm,
was performed at a 54 deg take-off angle by using a mono-
chromatized Al Kα x-ray source. Acceleration voltage of the
ion gun was either 500 V or 3 kV, while ion current was kept
at 12.5 μA/cm².

### 3 Results and Discussion

#### 3.1 PMMA Etching in Argon Plasma or Oxygen

Plasma

The etching rates and the PMMA/PS etching selectivity
in argon or oxygen plasmas are listed in Table 1. In the case
of both plasmas, etching rates of PMMA are higher than
those of PS. In the case of argon plasma, selectivity is
3.9, which is higher than that in the case of oxygen plasma,
which is 1.7. This result, namely that PMMA/PS etching
selectivity in argon plasma is higher than that in oxygen
plasmas, is consistent with recent experimental measurements
reported by Liu et al.\textsuperscript{12} and Ting et al.\textsuperscript{13}

In argon plasmas, physical sputtering by argon ions is
the main mechanism of etching. The high-etching selectivity
in argon plasmas is probably due to the difference between
the molecular structures of PS and PMMA. The schematics
of the molecular structures of PS and PMMA are illustrated
in Fig. 1. The molecular structure of PS includes benzene
rings, which enhance the durability of polymers against etch-
ing. The enhancement in the durability is due to π electrons
in these benzene rings.\textsuperscript{21} In contrast, the molecular structure
of PMMA includes oxygen atoms instead of benzene rings.
The oxygen atoms enhance the etching rate, because carbon
atoms in polymers are easily volatilized when oxygen atoms

<table>
<thead>
<tr>
<th>Etching rate (nm/min)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PS</td>
</tr>
<tr>
<td>Argon plasma</td>
<td>6.6</td>
</tr>
<tr>
<td>Oxygen plasma</td>
<td>18.4</td>
</tr>
</tbody>
</table>

### Table 1

Etching selectivity of PMMA/PS in argon and oxygen plas-
mas (100-W source power, 50-V FSV, 10-W bias power, 2.0-Pa gas
pressure, and 120-s etching time).
are present. This difference in the molecular structures of PS and PMMA is the cause of their different etching rates.

To investigate the argon plasma process in detail, time dependence of etching depth was evaluated (Fig. 2). The PMMA etching rate is reduced by more than one half after the etching depth exceeds 15 nm. If PS etching rate was constant regardless of etching depth, this result (i.e., over 50% reduction in etching rate) explains the low-etching selectivity and pattern degradation in formation of a PS mask with thickness of more than 20 nm.

### 3.2 Effect of Oxygen Impurities on PMMA Etching

One possible cause for the decrease in PMMA etching rate in argon plasma is the change in the amount of oxygen from the Al$_2$O$_3$ dome or the change in the amount of residual oxygen impurities, such as water or other adsorbates, on the chamber wall or on the surface of the wafer. The amount of oxygen incorporation is expected to be especially high immediately after plasma ignition. The time dependence of oxygen-emission intensity was determined by using a bare silicon wafer under argon plasma at high-source power (1000 W) and high-FSV (400 V) etching conditions (Fig. 3). According to the figure, the intensity of oxygen emission decreases with increasing time after plasma ignition. The high-oxygen intensity immediately after plasma ignition is probably due to the oxygen impurities that originate from the Al$_2$O$_3$ dome or residual oxygen impurities. It should be noted that oxygen emission did not change under low-source power (100 or 200 W) etching conditions, as shown in Table 1 and Fig. 2. However, a small amount of oxygen impurities, which was below the detection limit, was supposed to exist in the plasma under the low-source power etching condition.

Time dependence of etching depth with IBE was evaluated next. By using IBE, it was possible to avoid the etching-rate change (namely avoid the PMMA-etching-rate enhancement by oxygen impurities), because PMMA is etched only by argon ions when the PMMA and plasma (i.e., ion source) are separated. Furthermore, the etching-rate change due to variations in the ion-source condition can be suppressed by using IBE, because the shutter used in IBE does not open until the ion current reaches a stable value.

Time dependences of PMMA etching depth for IBE are shown in Fig. 4. According to the figure, etching depth increases linearly with increasing etching time until it reaches 26.7 nm, and the etching rate is reduced to less than one half of its initial value after the etching depth exceeds 26.7 nm. This result indicates that the change in concentration of oxygen impurities is not the cause of the reduction in etching rate.

### 3.3 Effect of Surface Oxygen on PMMA Etching

To identify the cause of the reduction in PMMA etching rate, the surface composition of PMMA was examined by XPS with an argon-ion gun. Oxygen-to-carbon (O/C) ratios are plotted in Fig. 5 as a function of argon-ion irradiation time. Acceleration voltage of the ion gun was either 500 V or 3 kV, while ion current was kept at 12.5 μA/cm$^2$. The O/C ratios...
were calculated from the narrow-scan spectra of O\textsubscript{1s} and C\textsubscript{1s}.

According to the figure, O/C ratio decreases with increasing ion-irradiation time. Moreover, the reduction of O/C ratio is more rapid under high-ion energy conditions (i.e., 3 kV). These results provide strong evidence that the reductions in etching rate for both argon plasmas and IBE are caused by the depletion of oxygen concentration by ion bombardment. This finding is consistent with a previous study, which showed that etching rate of organic materials decreases with decreasing O/C ratio.

To evaluate the PMMA/PS etching selectivity, the changes in O/C ratio due to argon-ion irradiation in the cases of PMMA and PS were compared (Fig. 6). Acceleration voltage of ion irradiation was 3 kV, ion current was 12.5 μA/cm\textsuperscript{2}, and irradiation time was 60 s. The O/C ratio of PMMA decreases from 0.35 to 0.026 after ion irradiation. On the other hand, the O/C ratio of PS is almost unchanged (i.e., decreases from 0.059 to 0.057). A small change in PS etching rate is therefore expected, because the change of O/C ratio of PS is much smaller than that of PMMA. The O/C ratio of PS is considered to be zero, because there is no oxygen in PS according to the PS molecular structure in Fig. 1(a). However, the peak of O\textsubscript{1s} in PS is observed by our XPS analysis, and the O/C ratio of PS does not become zero. The origin of oxygen is tentatively identified as oxygen absorbed during air exposure or oxygen existing as production impurities, such as lubricant or surfactant molecules, in the initial films. The PS film was etched in argon plasma for 300 s at 200-W source power, 5-W bias power, and 2.0-Pa gas pressure. PS etching depth was estimated to be 42.5 nm. On the assumption that PS etching rate is constant regardless of etching depth, high PMMA/PS etching selectivity, namely 6.9, is expected when the depth is below 15 nm. The lower etching rate of PS compared with PMMA is due to the difficulty in breaking the stable benzene ring to form volatile species, as described in Sec. 3.1.

The change in O/C ratio of PMMA is probably due to the change in oxygen composition that comes from the following two origins: One is the oxygen originally contained in the film, as shown in Fig. 1(b) and the other is the oxygen absorbed to the film surface during air exposure. To investigate the oxygen-composition change due to air exposure, the difference in the surface compositions before and after air exposure was evaluated. Two wide-scan spectra taken by XPS are shown in Fig. 7: one was taken immediately after 30-s argon-ion irradiation under 3-kV acceleration voltage and 12.5-μA/cm\textsuperscript{2} ion current and (b) wide-scan spectrum after 120-s air exposure.

To clarify the effect of air exposure on etching rate of PMMA, the time dependence of etching depth was evaluated. Measured etching depth in an ion-beam etched sample without any treatment before IBE is plotted in Fig. 8.

---

**Fig. 5** Time dependence of O/C ratio in the PMMA film measured by x-ray photoelectron spectroscopy (XPS) with argon-ion gun. Acceleration voltage of the ion gun was 500 V or 3 kV with constant ion current of 12.5 μA/cm\textsuperscript{2}.

**Fig. 6** Comparison of O/C ratio change by argon-ion irradiation of PMMA and PS. Irradiation conditions: 3-kV acceleration voltage, 12.5-μA/cm\textsuperscript{2} ion current, and 30-s irradiation time.

**Fig. 7** Comparison of wide-scan spectra of PMMA measured by XPS before and after air exposure: (a) wide-scan spectrum after 30-s argon-ion irradiation under 3-kV acceleration voltage and 12.5-μA/cm\textsuperscript{2} ion current and (b) wide-scan spectrum after 120-s air exposure.

**Fig. 8** Comparison of time dependence for two PMMA samples: (a) untreated sample before IBE and (b) etched sample by argon plasma before IBE. Etching time of argon plasma was 32 s (which is one of the points plotted in Fig. 2). Sample (b) was exposed to air for about 1 day between plasma etching and IBE.
Measured etching depth of an ion-beam etched sample that was etched by argon plasma before IBE is also plotted in the graph. The etching time in the case of the argon plasma was 32 s under 200-W source power, 50-V FSV, 5-W bias power, and 2.0-Pa gas pressure. These two samples were exposed to air for more than 1 day before IBE. Both etching depths show a similar dependence on IBE time. In particular, the slopes of etching depth up to 15 s are much steeper than those after 15 s. This finding suggests that surface-oxygen composition (i.e., O/C ratio) of the sample after 32-s plasma etching is depleted. However, etching depth rapidly increased during the early etching stage, even in the case of the sample with argon-plasma pretreatment. This result shows that the primary cause of etching-rate reduction is attributed not to the reduction in oxygen composition in the film, but to the reduction in oxygen absorbed by the film surface during air exposure. It should be noted that high PMMA/PS etching selectivity when the depth is below 15 nm may be unstable, because the amount of attached oxygen easily changes according to the storage condition.

### 3.4 Effect of Oxygen Addition to Argon Plasma

To avoid the change in PMMA/PS etching selectivity due to etching-rate change and variable storage conditions, a small amount of oxygen was added to the argon plasma. The time dependences of etching depth for a pure-argon plasma, argon plasma with 1% oxygen addition, and pure oxygen plasma are plotted in Fig. 9. Bias power was 5 W, and gas pressure was 2.0 Pa. In the case of pure oxygen plasma, plasma-source power was adjusted to ensure that the ion energy was the same as that in the case of the argon-based plasma. The samples etched in mixed argon-oxygen plasma and oxygen plasma only show linear dependences of etching depth on etching time, even when the etching depth exceeded 50 nm. This result indicates that the addition of a slight amount of oxygen to the argon plasma suppresses the variation in etching rate due to the depletion of oxygen concentration during plasma etching. The value of PMMA/PS etching selectivity in the case of the mixed argon-oxygen plasma was estimated to be 4.2 at 60-s etching time.

Etched fingerprint patterns of PS-b-PMMA, which have three kinds of patterns with full pitches, are shown in Fig. 10. The mixed argon-oxygen plasma was used to fabricate these patterns. It is clear from these images that fine PS mask patterns with a full pitch in the range of 25.5 to 77 nm were successfully formed with the mixed argon-oxygen plasma.

### 4 Concluding Remarks

Etching characteristics of argon-oxygen-based plasmas, which are promising for highly selective PMMA etching of PS-b-PMMA, were investigated. Time dependence of etching depth in argon plasma shows that etching rate decreases by more than half after etching to a depth of around 15 nm. The results of XPS analysis of the PMMA surface revealed that the reduction in etching rate is caused by a depletion of oxygen concentration by argon-ion bombardment. To compensate for the decrease in oxygen concentration, 1% oxygen was added to the argon plasma. As a result, PMMA etching rate was constant, even beyond the...
etching depth of 50 nm. Fine PS mask patterns with full pitches in the range of 25.7 to 77 nm were successfully formed by using the mixed argon-oxygen plasma. It is thus concluded that this mixed argon-oxygen plasma will provide selective PMMA/PS etching for next-generation nanoscale patterning.

References


Makoto Satake received his BS and MS degrees in applied physics from Tokyo University of Science, Tokyo, Japan, in 2004 and 2006, respectively, where he researched the method of ferroelectric-single-crystal growth. After graduation, he joined Hitachi’s Central Research Laboratory, Tokyo, in 2006, where he did research in plasma etching technique, especially for DSA etching and nonvolatile material etching.

Taku Iwase received his BS and MS degrees in materials science and engineering from Tohoku University, Miyagi, Japan, in 2007 and 2009, respectively, where he developed magnetic resistive device using Heusler alloy. After graduation, he joined Hitachi’s Central Research Laboratory, Tokyo, in 2009, where he did research in the areas of magnetic materials etching and DSA etching.

Masaru Kurihara received his BS, MS, and PhD degrees in electrical engineering from Keio University, Tokyo, Japan, in 1996, 1998, and 2001, respectively, where he developed the plasma simulator, especially for electron swarm and micro-cell plasma. After graduation, he joined Hitachi’s Central Research Laboratory, Tokyo, in 2001, where he did research in the areas of gate etching and metal etching. His main research interests are fab-wide process control and process modeling in a gate-module formation.

Nobuyuki Negishi was awarded his BE and ME degrees in precision engineering from Osaka University in Japan in 1994 and 1996 respectively, where he researched the characteristics of atmospheric pressure plasma. After his graduation, he commenced his career with Central Research Laboratory of Hitachi, Tokyo, in 1996, where he was responsible for development of etching systems and processes for semiconductor manufacturing. His main research area is especially profile evolution and its mechanisms.

Yasuhiko Tada has been a member of the research staff at Hitachi Research Laboratory, Hitachi Ltd., since 2004. He received his master’s degree in materials chemistry and his doctorate degree in polymer chemistry from Kyoto University in 2004 and 2012. His research interests focus on the self-assembled materials and structures of block copolymers for nanofabrication.

Hiroshi Yoshida received a Dr. Eng. degree in polymer chemistry from Kyoto University in 1992. From 1993 to 1998, he joined Hashimoto Polymer Phasing Project, ERATO, Japan Science & Technology Corporation (JST), as a research scientist. In 1998, he moved to Hitachi Research Laboratory, Hitachi Ltd. His current interest includes directed self-assembly processes for next generation nano-scale electronic and biodevice fabrication. He is a member of American Chemical Society.