Substrate-Effect of Chemically Amplified Resist

Shigeyasu Mori, Kouichirou Adachi, Takashi Fukushima, and Yuichi Sato
Central Research Laboratories, Sharp Corporation,
2613-1, Ichinomoto-cho, Tenri-shi, NARA Pref. 632, JAPAN

SiN, Bare Si, and SiO2 substrate-effects in chemically amplified (CA) resist have been investigated by surface analysis and evaluating the pattern profile of CA negative tone resist. It is considered that substrate-effects are distinguished from adhesion, optics and substrate components. It is found that the undercut profile of negative tone resist on SiN substrate can not be due to adhesion and optics. Fine profile can be replicated on SiN substrate treated with oxygen plasma optimized condition. Undercut profile can not be affected mainly by adsorbed materials on SiN substrate from Thermal Desorption Spectroscopy (TDS) analysis results. From the results of Electron Spectroscopy for Chemical Analysis (ESCA), it is found that Si-N bonding is replaced to Si-O bonding while SiN substrate is treated with oxygen plasma. The pattern profile on SiN substrate by oxygen plasma treatment is improved by the thin SiO2 layer formed on SiN substrate. Relations between footing length and oxygen plasma treatment condition suggest that undercut profile is caused by the atom content of nitrogen on the surface of SiN substrate. Excessive oxygen plasma treatment of SiN substrate occurs the footing profile for the negative tone resist because of surface damage. At the interface between the SiN substrate and the CA resist, the SiN substrate works as base existing H2O, and quenches photo-generated acids. Additionally, it is considered that the NHX on SiN substrate quenches the photo-generated acids directly. The mechanism of substrate-effect is clarified.

1. INTRODUCTION
CA resist for single layer lithography using KrF excimer laser can provide the high performance required for fabrication of quarter-micron feature size and below LSI[1]. Also, they are expected to be used in ArF excimer laser, electron beam and X-ray lithography. Acid which was generated by photo-induced reactions in CA resist is environmental instable[2]. In order to establish stable lithographic processing of CA resist, resist processing and resist materials are improved. In the resist processing, it is proposed to apply a protective overcoat[3,4] and to purify atmosphere by ammonia adsorption filter[5]. For resist materials, the reduction of free volume in resist film and the incorporation of stabilizing additive are proposed[6]. Stable CA resist processing becomes to be acceptable for manufacturing purpose[7].

The resist pattern profile of CA resist can take the form of footing in positive tone resist and undercut in negative tone resist, at the interface between resist and SiN substrate[8,9,10]. Those problems were observed on several materials for substrates, for examples Spin On Glass (SOG)[11], TiN[12,13] and plasma-chemical-vapor-deposited SiO2[14]. It was reported that SiN substrate treated with oxygen plasma is effective to improve pattern profile[9]. It is important to clarify the mechanism for reduction of substrate-effect. The effect is considered to be complex, we separate it from a few parts. The first part is adhesion, the characteristics of adhesion between inorganic substrates and novolac-DNQ resist has been reported[15]. The second part is optical
effect from substrate structure, we analyze this by lithographic simulation. The third part is substrate component, we evaluate the pattern profile formed on the substrate with several plasma treatments. The substrate-effect is investigated by surface analyzing technique which is Thermal Description Spectroscopy (TDS) and Electron Spectroscopy for Chemical Analysis (ESCA).

2. EXPERIMENTAL

SiN substrate was prepared with low pressure chemical vapor depositing on the silicon dioxide (SiO2) film which was formed by pyrooxidation on Si substrate. SiN film thickness is 120 nm, and SiO2 film thickness is 28 nm. SiN substrate was treated with oxygen plasma at the room temperature using ANELVA model ECR6011 equipped substrate RF bias with the base pressure of 3 mtorr. Substrates were primed with hexamethyl-disilazane(HMDS) and then coated with the CA negative tone resist PEX-212 (Sumitomo Chemical Co. Ltd.), C04 (Mitsubishi Chemical Co. Ltd.) and CA positive tone resist APEX-E (Shipley Far East Ltd.). The resist thickness is 0.7 μm for PEX-212 and APEX-E and 1.0 μm for C04. Exposure was carried out by utilizing a deep-UV stepper (NA =0.45) equipped with a KrF excimer laser light source. Then post exposure bake was carried, and developing was treated in the solution of tetramethyl ammonium hydroxide aqueous base, and rinse was treated in the water. Developed images were observed on a Hitachi model S-900 scanning electron microscope (SEM). Footing length is evaluated from SEM photograph of resist pattern profile. It was utilized Shimazu model ESCA3200 of Electron Spectroscopy for Chemical Analysis (ESCA). Substrate contamination was evaluated by thermal desorption spectroscopy (TDS) using ESCO model EMD-WA1000K. Before the resist coating and the surface analysis, substrates were cleaned with HF solution to avoid impurity adsorption during the storage time between the SiN-deposition and the oxygen plasma treatment on the substrate surface[9]. Contact angle was measured with Shimazu model ST-1. Lithographic simulation was done using TMA model depict-2.

3. RESULTS and DISCUSSION

3.1 Pattern profile and Adhesion

It is shown that the CA negative tone resist pattern profile was undercut on SiN substrate, shown in Figure 1. Also, resist pattern profile on bare silicon is footing. It is expected that

![SEM photographs of pattern profiles on different substrates](image_url)

Fig. 1. SEM photographs of 0.30 μm line and space negative tone resist (C04) pattern profiles on bare Si with HMDS(a), SiN with HMDS (b), SiO2 with HMDS (c), bare Si without HMDS(d), SiN without HMDS (e) and 0.26 μm line and space pattern profile on SiO2 without HMDS (f).
undercut and footing profile may be due to adhesion between substrate and CA resist. In order to evaluate the adhesion of substrates, the contact angles of water on each substrate are shown in Table 1. The contact angles on substrates without HMDS treatment are different, but that with HMDS treatment are almost same. Considering relation between the pattern profiles and the contact angles, the resist pattern lies down on the substrates having lower contact angle. It is considered that a contact angle can affect the adhesion of resist pattern, can not be due to undercut and footing profiles.

### 3.2 Relationship between the oxygen plasma treatment and resist pattern profile

Figure 2 shows the pattern profiles of another type of negative tone resist. The resist patterns on SiN substrate lie back on other patterns and its profile is undercutted. Also, resist pattern profile on bare silicon is footing. On the other hand, the positive tone resist pattern on SiN substrate is footing, shown in Figure 2(c). It suggests that photo-generated acids are quenched by SiN substrate. It is reported that oxygen plasma treatment by using asher of the down flow type is effective preventing from acids deactivation[9]. In this study, relation between the footing length of CA negative tone resist pattern profile is evaluated changing the condition of oxygen plasma treatment by etcher equipped substrate RF bias. The mechanism of SiN substrate-effect in CA resist is investigated. Figure 3 shows the pattern profiles on SiN substrate treated with oxygen plasma at several RF power conditions. Resist pattern on SiN substrate treated with oxygen plasma at RF power condition of 0 W is formed with undercut and it is not lying down. For RF power condition of 240 W, resist pattern profile has no undercut and footing. It is obvious that resist pattern profile is controlled by RF power in the oxygen plasma treatment.

In order to estimate the footing effect, we used the resist footing length described in Figure 4. Relation between the footing length for 0.26 µm and 0.30 µm of 1:1 periodic line and space pattern of CA resist and the RF power condition of the oxygen plasma treatment for 60 seconds on SiN substrate is shown in Figure 5. Undercut profile was observed on SiN substrates for the RF power condition of 0 W to 120 W in oxygen plasma treatment. Fine profile can be replicated at the RF power condition of 240 W in oxygen plasma treatment. Resist patterns were formed on SiN substrate treated with oxygen plasma changing treatment time at constant RF power condition of 30 W and 120 W, shown in figure 3(c)(d)(e)(f). Summarized relation between the footing length of the CA negative tone resist pattern profile and the oxygen plasma treatment time on SiN substrate for the RF power condition of 30 W and 120 W is shown in Figure 6. For the RF power condition of 30 W, it is recognized that footing length is saturated at -30 nm to -50 nm from 60-seconds treatment to 600-seconds treatment. For the RF power condition of 120 W, footing profile was

### Table 1 Contact angle of water on the substrate.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Pretreatment</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare Si</td>
<td>non</td>
<td>75.5</td>
</tr>
<tr>
<td>SiO2</td>
<td>non</td>
<td>2.3</td>
</tr>
<tr>
<td>SiN</td>
<td>non</td>
<td>29.0</td>
</tr>
<tr>
<td>bare Si</td>
<td>HMDS</td>
<td>73.2</td>
</tr>
<tr>
<td>SiO2</td>
<td>HMDS</td>
<td>65.4</td>
</tr>
<tr>
<td>SiN</td>
<td>HMDS</td>
<td>50.3</td>
</tr>
</tbody>
</table>
observed on SiN substrates of oxygen plasma treatment longer than 400-seconds-treatment, undercut profile was observed from 0-seconds treatment to 60-seconds treatment. Fine profile be replicated observed by oxygen plasma treatment for 180 seconds. The pattern profile of CA negative tone resist can be controlled by the condition of the oxygen plasma treatment. It is obvious that the resist pattern profile on SiN substrate depends on oxygen plasma treatment condition complicatedly. It can be considered that the undercut and the footing due to the interaction between photo-generated acid and SiN substrate.

Fig. 3. SEM photographs of 0.30 µm line and space negative tone resist (PEX-212) pattern profiles on SiN treated with oxygen plasma at RF power condition of 0 W for 60 seconds (a), 240 W for 60 seconds (b), 30 W for 60 seconds (c), 30 W for 600 seconds (d), 120 W for 60 seconds (e) and 120 W for 600 seconds (f).

observed on SiN substrates of oxygen plasma treatment longer than 400-seconds-treatment, undercut profile was observed from 0-seconds treatment to 60-seconds treatment. Fine profile be replicated observed by oxygen plasma treatment for 180 seconds. The pattern profile of CA negative tone resist can be controlled by the condition of the oxygen plasma treatment. It is obvious that the resist pattern profile on SiN substrate depends on oxygen plasma treatment condition complicatedly. It can be considered that the undercut and the footing due to the interaction between photo-generated acid and SiN substrate.

Fig. 4. Calculation used to determine footing length.

Fig. 5. Relation between footing length of CA negative tone resist and RF power condition of oxygen plasma treatment for 60 seconds on SiN substrate.
3.3 Optical effect of substrate thickness

A optical effect from substrate structure is considered to clarify the cause of the footing and undercut profile. It is expected that CA resist pattern profile depends on the film components and their thicknesses of substrate because of high transparency of CA resist. The pattern profile on SiN substrate having several film thickness is evaluated. SiN substrates were prepared with low pressure chemical vapor depositing on SiO2 (28 nm). In order to study optical effect from substrate only, we have to eliminate the acids quenching by SiN substrate. And all SiN substrates treated with oxygen plasma for 180 seconds by using asher of the down flow type. Relation between the footing length 0.30 μm of 1:1 periodic line and space pattern of negative tone CA resist (PEX-212) and SiN film thickness, and relation between footing length calculated by lithographic simulation and SiN film thickness, are shown in figure 7. It is found that the footing length has the maximum value at 100 nm while the results of patterning is equivalent to that of simulation. The patterning results agree with simulation. Footing length of SiN substrate with 120-nm thickness is -30 nm. The saturated footing length shown in figure 6 for RF power condition of 30 W can be considered to be due to optical effect of substrate structure. But this agreement can not explain that the pattern of RF power condition of 120 W in figure 6 shows footing profile from 400-seconds to 600-seconds.

3.4 Analysis of substrate treatment by thermal desorption spectroscopy (TDS)

From the above results, the undercut profile on SiN substrate is understood not to be affected by adhesion and optics. It can be expected that the undercut profile on SiN substrate due to the base contaminations. In order to identify the contamination on SiN-substrate surface, TDS analysis carried out for SiN substrate cleaned with HF solution and treated with oxygen plasma. TDS was carried out from the temperature of 50 °C to 1000 °C at the heating rate of 1 °C/seconds, after the base pressure was evacuated to less than 10⁻⁹ torr. The spectra for molecular weight of 16, 17 and 18 were measured.

The relation between the ion intensity and desorption temperature of SiO2 substrate formed by pyrooxidation is shown in Figure 8(a). Desorption curves for molecular weight of 16, 17 and 18...
are all quite similar and peaks appear at 350 °C. This indicates the SiO$_2$ substrate adsorbed H$_2$O. TDS spectra of the SiN substrate treated with oxygen plasma at the RF power conditions of 120 W for 30 seconds are similar to those of the SiO$_2$ substrate shown in Figure 8(b). This suggests that the surface of SiN substrate treated with oxygen plasma become like a SiO$_2$ surface. Figure 8(c) shows TDS spectra of the SiN substrate cleaned with HF solution. The spectrum for molecular weight of 18 has peak at 350 °C and shoulder at 220 °C. The spectra for molecular weight of 16 and 17 have peaks at 350 °C. It can be considered that the part of the desorption ion due to H$_2$O. It is necessary to discuss that molecular weight of 16, 17 and 18 may be caused by NH$_x$, for example that of 16 for NH$_2$, that of 17 for NH$_3$, that of 18 for NH$_4$. But, it is difficult to separate these spectra of H$_2$O and NH$_x$. The volume of desorption gas of SiN substrate cleaned with HF solution is half of SiN substrate treated with oxygen plasma. This suggests that the undercut profile can not be affected mainly by adsorbed materials on substrate.

3.5 Analysis of SiN surface by Electron Spectroscopy for Chemical Analysis (ESCA)

In order to investigate the effect of oxygen plasma, we utilized ESCA. Figure 9 shows ESCA spectra of SiN substrate cleaned with HF solution and treated with oxygen plasma. It is found that there are more oxygen atoms and fewer nitrogen on the surface of SiN substrate treated with oxygen plasma, comparing with SiN substrate cleaned with HF solution. Further, atom contents for SiN substrate are calculated with dividing spectrum of Si(2p) into Si-N bonding and Si-O bonding. Relation between atom contents and RF power condition is shown in Figure 10. An amount of Si-O
bonding and oxygen atoms increased, while that of Si-N bonding decreased depending on RF power condition of oxygen plasma treatment. Figure 11 and Figure 12 show atom contents depending on oxygen plasma treatment time at the RF power condition of 30 W and 120 W, respectively. For the RF power condition of 30 W, an amount of oxygen atoms and Si-O bonding increased, while that of Si-N bonding decreased gradually during the oxygen plasma treatment. This indicates that Si-N bonding is replaced to Si-O bonding by oxygen plasma. For the RF power condition of 120 W, all atom contents have a tendency to the RF power condition of 30 W beyond

![Graph](image)

**Fig. 9.** ESCA spectra of SiN substrate cleaned with HF solution and treated with oxygen plasma for 30 seconds at RF power condition of 120 W.

**Fig. 10.** Relation between atom content of SiN substrate surface and RF power condition of oxygen plasma treatment on SiN substrate.

![Graph](image)

**Fig. 11.** Relation between atom content of SiN substrate surface and oxygen plasma treatment time for RF power condition of 30 W on SiN substrate.

![Graph](image)

**Fig. 12.** Relation between atom content of SiN substrate surface and oxygen plasma treatment time for RF power condition of 120 W on SiN substrate.
30 seconds oxygen plasma treatment. An amount of Si-N bonding is saturated from 60 seconds to 180 seconds oxygen plasma treatment, and increased above 180-seconds oxygen plasma treatment. Above 60-seconds oxygen plasma treatment, an amount of oxygen atoms and Si-O bonding decreased, while Si-N bonding increased because of kinetic damage on the surface of substrate by the oxygen plasma treatment. It can be considered that Si-N bonding is replaced to Si-O bonding within 30 seconds oxygen plasma treatment equivalently to the case of the RF power condition of 30 W.

3.6 Pattern profile on SiN treated with SF₆ plasma.

The cause of the footing profile observed in figure 3(f) have not been clarified yet. It is expected that SiN surface is roughened by oxygen plasma. In order to investigate the effect of surface roughness, SiN substrate was treated with SF₆ plasma to etch the surface using ECR6011. The resist pattern profile is undercut, shown in figure 13(a). The SiN substrate was cleaned with HF solution after SF₆ plasma treatment to eliminate SiO₂ layer formed by other plasma species. The 0.38 μm line and space resist pattern having undercut is formed, shown in figure 13(b). A pattern of size below 0.36 μm was not formed on the substrate at all. Above footing profile can not be due to surface roughness, on the contrary, the roughness promote acids-quenching by SiN substrate. It is suggested that this supports the mechanism of acid-quenching by SiN substrate. Figure 13(c) shows the pattern profile on SiN substrate oxidized thermally. The footing profile can not be observed. This resist profile is similar to that of figure 3(c)(d). This suggested that the surface of SiN substrate treated with oxygen plasma at RF power condition of 30 W changes to like a SiO₂. Thin SiO₂ layer is formed on SiN substrate by oxygen plasma shown in figure 14(a), and the layer prevents from acids-quenching by SiN substrate.

![Fig. 13. SEM photographs of 0.30 μm line and space negative tone resist (PEX-212) pattern profiles on SiN substrate treated with SF₆ plasma for 10 seconds (a), 0.38 μm line and space profiles on SiN substrate cleaned with HF solution after SF₆ plasma treatment for 10 seconds (b) and 0.30 μm line and space profiles on SiN substrate oxidized at 1050 °C for 33 minutes (c).]

3.7 Mechanism of undercut and footing profile on SiN substrate.

In previous study, it is shown that the terminated hydrogen on bare Si dissociates easily into resist, and occurs the footing profile of CA negative resist[8]. The negative tone resist pattern formed on SiN substrate treated with oxygen plasma at RF power condition of 120 W for 600 seconds (see figure 3(f)) is similar to that formed on bare Si (see figure 2(a)). These profiles are footing. On SiN substrate treated with oxygen plasma at RF power condition of 120 W for 600 seconds, the bond of Si is damaged by excessive oxygen plasma treatment, and the damaged Si bond is terminated by hydrogen, shown in figure 14(b). It can be considered that this mechanism occurs the footing profile.

On the other hand, it is reported that the photo-generated acids are trapped on unshared electron pair of nitrogen on SiN surface[8]. Considering both resist pattern profile and ESCA results, undercut profile can be due to nitrogen of SiN substrate surface. Using TDS results, there is H₂O on SiN substrate cleaned with HF solution. We provide that the photo-generated acids quenching
process on the surface on SiN substrate, shown in scheme 1. At the interface between the SiN substrate and the CA resist, the SiN substrate works as base existing H₂O. The proton dissociated from the H₂O at the interface is trapped on SiN surface, and the photo-generated acid is neutralized by OH⁻. Contents of nitrogen atom and silicon atom of the Si-N bonding of the SiN substrate cleaned with HF solution are 42 % and 36 %, respectively shown in Figure 11. The atom content of nitrogen and silicon of SiN substrates treated with oxygen plasma are same values, or nitrogen atoms content smaller than silicon one. The ratio of nitrogen atoms to silicon atoms decrease, while the atom content of nitrogen decrease dramatically. It is considered that the atom content of nitrogen on surface and the surface structure relates with pattern profile of CA resist. This supports above mechanism.

Secondly, there is the adsorbed NHₓ on SiN substrate from TDS results. It can be understood that the NHₓ working as base quenches the photo-generated acids directly, shown in scheme 2. It is considered that the reaction quenching the photo-generated acids is complex.

4. CONCLUSION

For chemically amplified, we investigate the substrate effect of CA resist on SiN, bare Si and SiO₂ substrate. Resist patterns are formed on substrates depending on adhesion, optics and surface component. Resist pattern profile on SiN substrate can be optimized by the oxygen plasma treatment. Fine profile is replicated on SiN substrate treated with a parameter of oxygen plasma.
Thin SiO$_2$ layer is formed on SiN substrate by oxygen plasma treatment, and the pattern profile is improved. Undercut of resist pattern can be affected mainly by the adsorbed materials on SiN substrate, and can be caused by nitrogen on the surface of SiN substrate. It is considered that the photo-generated acids are quenched by SiN substrate working as base existing H$_2$O and that they are quenched by NH$_X$ directly.

5. ACKNOWLEDGMENT
The authors express their gratitude to Y. Nakao and T. Mukai for their technical advises. They would like to thank Dr. N. Hashizume (Sharp CRL General Manager) and Dr. Y. Nakajima (Sharp CRL Deputy General Manager) for their continuous encouragement during this work.

6. REFERENCES