Removal of Ion Implanted Resists with Various Acceleration Energy using Wet Ozone

Yousuke Gotoa, Takeshi Maruokaa, Masashi Yamamotoa, Hideo Horibeac, Eiji Kusanoa, Toshinori Miurab, Mituru Kekurab and Seiichi Tagawaac

a. Research Laboratory for Integrated Technological Systems, Kanazawa Institute of Technology, Yatsukahoh, Hakusan, Ishikawa 924-0838, Japan
b. Core Technology Research & Development Center, Meidensha Corporation, 515 Kaminakamizo, Higashimakadod, Numazu, Shizuoka 410-8588, Japan
c. The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka, Ibaraki, Osaka 567-0047, Japan
E-mail: hhoribe@neptune.kanazawa-it.ac.jp

We investigated the removal of ion-implanted resists with various acceleration energy using wet ozone. The resist removal rate decreased with increasing acceleration energy in B- and P-ion-implanted resists. The hardness of ion-implanted resists increased with increasing acceleration energy as a result of nanoindentation, and was simulated by Stopping and Range of Ions in Matter software (SRIM2008).

Keywords: resist, removal, wet ozone, acceleration energy, environment.

1. Introduction

Resist removal from substrates in a semiconductor manufacturing process conventionally makes use of oxygen plasma or the mixture of sulfuric acid and hydrogen peroxide. A recent issue regarding the resist removal process has been focused on the high running costs using expensive chemicals and their environmental impact. Ozone is expected to replace conventional cleaning processes for removal the resist and organic residue because of its high oxidation potential. Using ozone instead of chemicals also has the advantage of reducing both the environmental impacts and the amount of water necessary for chemical washing. Dry ozone gas was firstly applied to resist removal at an elevated temperature range [1-3]. The dry process by ozone requires that the resist is removed from the substrate as a volatile compound such as water vapor and/or carbon dioxide. Since the resist is not completely oxidized by the ozone itself, the process requires temperatures higher than 250°C to remove the resist, in order to generate sufficient more highly excited oxygen radicals from the ozone by thermal decomposition.

In the wet ozone process, water vapor condenses in a film at a temperature lower than 100°C, and the resist is partially oxidized to carboxylic compounds by the ozone and the condensed water [4]. We tried to remove the ion-implanted resists with various acceleration energy using wet ozone. We also measured load-to-depth of ion-implanted resist using nanoindentation [5]. Finally, we simulated the distribution of ions implanted in the resist using SRIM2008 [6].

2. Experimental

2.1. Removal of ion-implanted resist using wet ozone

Figure 1 is a diagram of the experiment apparatus for wet ozone (Mitsubishi Electric Corp. and SPC Electronics Corp.). Ozone gas mixed with a trace amount of water (wet ozone) is generated by bubbling ozone gas through hot water. Also, a trace amount of water attaches to the resist due to the
The difference in temperature ($T = T_1 - T_2$) between wet ozone ($T_1$) and Si wafer ($T_2$). The amount of water attached to the resist was controlled by adjusting this temperature difference [7]. In resist removal using wet ozone, the carbon-carbon double bond in the benzene ring of the resist reacts with the ozone to generate ozonide, which reacts with the water to generate carboxylic acid [8]. Finally, the carboxylic acid was washed down from the Si wafer by a pure-water (rinse).

Fig. 1. Experiment apparatus for the resist removal using wet ozone

Three treatments (wet-ozone irradiation, pure-water washing, and drying) were repeated in each cycle of the removal using wet ozone. The resist removal rate was calculated by dividing the initial resist thickness by the wet ozone irradiation time which the resist was removed completely. The cycle consisted of 10s at 2000rpm for wet-ozone irradiation, 5s at 2000rpm for pure-water washing, and 20s at 1000rpm for drying. The ozone gas density and flow rate were 230g/m$^3$ (10.2vol%) and 12.5slm. The wet ozone temperature was $T_1=60^\circ\text{C}$, and the Si wafer temperature was $T_2=50^\circ\text{C}$. In this study, the ion-implanted resist was a positive-tone novolak resist (AZ6112; AZ-Electronic Materials) with B- and P- ions were implanted at a dose of $5 \times 10^{13}$ atoms/cm$^2$, at each acceleration energies (10keV, 70keV and 150keV).

2.2. Measurement of ion-implanted resist using nanoindentation

We measured the indentation depth which the indenter was indented at a set load using nanoindentation (ENT-1040; ELIONIX). We examined the indentation depth by varying the maximum load from 1 to 15mgf. The loading rate was at 1/2000 of loads more than 8mgf, and at 0.004mgf/ms (lower limit) below 8mgf. We used a Berkovich-type diamond indenter with an apex angle of 115$^\circ$.

2.3. Ion implantation simulations using SRIM

We simulated the distribution of ion in resist using SRIM2008. The acceleration energies were 10keV, 70keV and 150keV. We used polymethyl methacrylate (PMMA) as the resist.

3. Results and Discussions

3.1. Removal of ion-implanted resist using wet ozone

We removed the ion-implanted resists with various acceleration energy at a dose of $5 \times 10^{13}$ atoms/cm$^2$ using wet ozone. Figure 2 plots the results of the removing ion-implanted resists using wet ozone. Table 1 presents the removal rate for ion-implanted resists with various acceleration energy. In the B- and P-ion-implanted resists, the removal rate decreased with increasing acceleration energy. Therefore, the resist removal rate would decrease with increasing hardness of the ion-implanted resist due to the increasing acceleration energy.

Fig. 2. Dependence of ion-implanted resist thickness on wet ozone irradiation time

3.2. Hardness of ion-implanted resists with various acceleration energy

Figure 3 presents the relationship between load and the indentation depth. In the B- and P-ion-implanted resists, the loading curve (Plotting load against indentation depth) increased in the order of 10keV<70keV<150keV. Table 2 lists the indentation depths at 10mgf. When the same load was applied to the resist, the indentation depth

![Fig. 1. Experiment apparatus for the resist removal using wet ozone](image-url)
Table 1. Removal rate of ion implanted resists with various acceleration energy

<table>
<thead>
<tr>
<th>Resist sample</th>
<th>Removal rate [µm/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B ions (10keV)</td>
<td>1.09 ± 0.08</td>
</tr>
<tr>
<td>B ions (70keV)</td>
<td>1.04 ± 0.08</td>
</tr>
<tr>
<td>B ions (150keV)</td>
<td>0.97 ± 0.07</td>
</tr>
<tr>
<td>P ions (10keV)</td>
<td>1.10 ± 0.08</td>
</tr>
<tr>
<td>P ions (70keV)</td>
<td>1.07 ± 0.08</td>
</tr>
<tr>
<td>P ions (150keV)</td>
<td>0.96 ± 0.06</td>
</tr>
</tbody>
</table>

decreased with increasing acceleration energy. Therefore, the resist hardness increases with increasing acceleration energy. Accordingly, in B- and P-ion-implanted resists, the resist removal rate decreased in the order of 10keV<70keV<150keV.

3.3. Distribution of implanted B-, P-ions in the resist

Figure 4 presents the distribution of implanted B- and P-ions in the resist. Implanted ions were distributed deeper in resist with increasing acceleration energy in B- and P-ion implanted resists. Resist resin may harden due to thermal cross-linking and/or carbonization when ions are implanted into the resist. Accordingly, the hardness of the resist increased with increasing acceleration energy. Therefore, the resist removal rate decreased in the order of 10keV>70keV>150keV.
4. Conclusion
We investigated the removal of ion-implanted resists with various acceleration energy using wet ozone.
(1) B- and P-ion implanted resist at a dose of $5 \times 10^{13}$ atoms/cm$^2$ were removed at all acceleration energy (10keV, 70keV, 150keV).
(2) The resist removal rate decreased in the order of 10keV>70keV>150keV.
(3) The hardness of ion-implanted resists increased with increasing acceleration energy by result of nanoindentation.
(4) The resist removal rate may decrease with increasing thickness of hardened resist by increasing acceleration energy.

Acknowledgment
Part of this study was supported by the New Energy and Industrial Technology Development Organization (NEDO) of Japan, Mitsubishi Electric Corporation and SPC Electronics Corporation.

References
5) A. Nakaue and N. Kawakami, Kobe Steel Engineering Reports, 52, 74-77 (2002)